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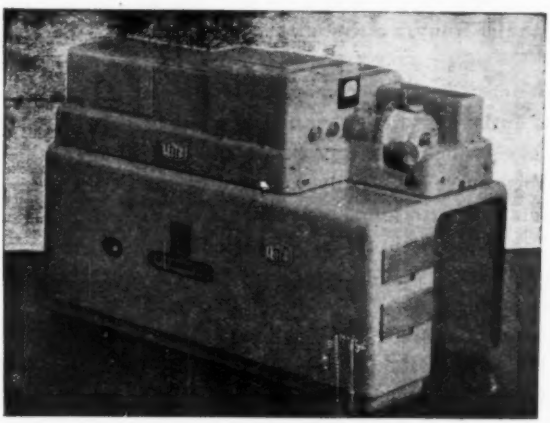

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[Jour. Indian Chem. Soc., Vol. 35, No. 11, 1958]

STUDIES IN CATALYTIC REACTIONS OF CHARCOAL. PART I. CATALYTIC OXIDATION AND DECOMPOSITION OF SALT SOLUTIONS

By Balwant Rai Puri, Lekh Raj Sharma and D. D. Singh

The catalytic oxidation of sodium nitrite, potassium arsenite, sodium sulphite and potassium ferrocyanide by atmospheric air and decomposition of sodium bicarbonate and sodium thiosulphate in the presence of the variously treated samples of sugar charcoal have been studied in some details. The maximum activity shown by the original sample has been ascribed to the presence of surface oxygen complex, capable of evolving carbon dioxide on degassing and of imparting acid character to the charcoal surface. A reasonable explanation for such reactions has been suggested.

Calvert (*J. Chem. Soc.*, 1867, **20**, 293) was probably the first investigator to demonstrate the catalytic oxidation of substances like alcohol, ethylene and hydrogen sulphide in the presence of charcoal. Feigl (*Z. anorg. Chem.*, 1921, **119**, 305) described similar catalytic oxidations of some inorganic salts. Krause (*Przemyst Chem.*, 1950, **29**, 377) attributed the catalytic activity of charcoal to the presence of impurities such as compounds of iron, calcium and magnesium. Kolthoff (*J Amer. Chem. Soc.*, 1932, **54**, 4473) and King (*J. Chem. Soc.*, 1935, 889) studied the catalytic oxidation of potassium ferrocyanide by atmospheric air in the presence of charcoal, prepared from the same sample but activated severally at temperatures varying from 400° to 950°, and while the former reported that the maximum activity was associated with the sample activated at 900° and minimum with that activated at 400°, the latter found the reverse to be the case. The reason for these anomalous observations was that Kolthoff's oxidations were carried out in buffer solutions which counterbalanced the alkaline nature of the high-temperature activated charcoals. It was not realised that the acidity or alkalinity of surface might be an essential factor, affecting the course of such reactions. As regards the catalytic decomposition of hydrogen peroxide, it was found by King (*loc. cit.*) that maximum activity was associated with the sample activated at 850° and minimum with that activated at 400°.

Bente and Walton (*J. Phys. Chem.*, 1943, **47**, 329) and Watanabe and Shiramoto (*J. Electrochem. Soc., Japan*, 1952, **20**, 386) have also reported that the catalytic activity of charcoal depends upon the nature of the treatment given to it as well as the temperature and the reagents used for activation. The catalytic activity has also been ascribed by some workers (Feigl, *loc. cit.*; Brinkmann, *Angew. Chem.*, 1949, **61**, 378; Courty, *Bull. Soc. Chim.*, 1947, 642; *Compt. rend.*, 1945, **221**, 27) to the film of adsorbed oxygen on the charcoal surface.

The influence which the oxygen complexes exercise on the surface behaviour of charcoal has been well known for some time (Puri *et al.*, *J. Phys. Chem.*, 1958, **62**, 756; *Ind. Eng. Chem.*, 1958, **50**, 1071; King, *J. Chem. Soc.*, 1937, 1489; Weller and Young, *J. Amer. Chem. Soc.*, 1948, **70**, 4155). Since catalytic reactions are, in the main, surface reactions, their study in the presence of charcoal, coated with different

types of oxygen complexes, is likely to be useful in elucidating the mechanism of such reactions. The present work was therefore undertaken with that end in view. It is divided into two parts ; the first part describes the catalytic oxidation and decomposition of some inorganic salts in aqueous solutions and the second part deals with the catalytic decomposition of hydrogen peroxide.

Experimental

Charcoal samples.—A sample of sugar charcoal, prepared by the carbonisation of cane sugar by means of sulphuric acid followed by repeated washings with distilled water, was used. It was divided into three portions: one portion was used as such and was labelled as 'original charcoal'. The other two portions were degassed, one at 750° and the other at 1200°. The amounts of the chemisorbed gases present in each sample were determined by evacuating them at 1200° and analysing the gases evolved in the Orsat-Lunge gas analysis apparatus. The results are recorded in Table I. It is seen that while the original sample contains oxygen disposed as CO and CO_2, that degassed at 750° contains oxygen disposed as CO only, and that degassed at 1200° does not contain any combined oxygen at all. The p_H value of the charcoal was seen to increase from 2.85 to 8.78 on degassing at increasing temperatures.

Table I

Amounts of gases evolved (mg./g.) *on evacuating different samples of sugar charcoal at* 1200° *together with their* p_H *values.*

Samples.	CO_2.	CO.	H_2O.	H_2.	p_H values.
Original sample	13.27	13.12	10.34	14.96	2.85
Sample degassed at 750°	Nil	9.76	4.69	12.87	7.20
Sample degassed at 1200°	Nil	Nil	Nil	Nil	8.78

Procedure.—Each sample (1 g. portion) was shaken mechanically with 100 c.c. of 0.1*N* solution each of sodium nitrite, sodium sulphite, potassium arsenite, potassium ferrocyanide, sodium thiosulphate and sodium bicarbonate for different intervals of time after which an aliquot portion of the clear supernatant liquid was analysed by suitable volumetric methods. A blank run, without the addition of charcoal, was made simultaneously in every case.

Table II

Catalytic oxidation of sodium nitrite by different samples of sugar charcoal.

	Percentage oxidation			
		With charcoal samples.		
Time of shaking.	Without charcoal.	Original.	Degassed at 750°.	Degassed at 1200°.
2 hrs.	0.32	39.00	0.63	0.62
4	0.63	53.12	0.94	0.93
8	0.94	57.56	1.56	1.58
12	1.56	62.50	1.88	1.88
24	1.80	73.26	2.10	2.23

Discussion

Taking the oxidation of sodium nitrite (Table II) in the first instance, it is seen that while in the absence of charcoal the reaction proceeds only to a small extent, in the presence of the original sample of charcoal, the reaction progresses considerably, the amount oxidised even within the first 2 hours being nearly 40% of the total amount of sodium nitrite taken. The reaction continues exponentially and within 12 hours more than 60% of the nitrite is oxidised. It may be mentioned that the amount of air contained in the empty space of the bottles, which remained corked during the reaction, was about 175 c.c. Thus, approximately 35 c.c. of oxygen was available for the reaction. This, as can be shown by simple calculations, could oxidise 6.4 m.e. (*i.e.* about 64% of the total amount added) of sodium nitrite only. The reason for the reaction to slow down after some time therefore appears to lie in the limited availability of oxygen. In a few experiments, the bottles containing the reaction mixtures were occasionally opened for a while to permit the frequent renewal of air. It was found that now practicaliy the whole of the nitrite could be oxidised. It appears therefore that the original sample of charcoal, containing oxygen complexes (Table I), can initiate a sort of a chain reaction which progresses further and further with time provided that a sufficient amount of oxygen is available.

The charcoal sample, degassed at 750°, which contained some oxygen disposed as CO but none as CO_2, and that degassed at 1200°, which did not contain any combined oxygen at all, could not bring about this oxi lation reaction to any noticeable extent (Table II). The p_H value of the original sample was 2.85 and those of the evacuated samples were 7.2 and 8.8. It appears that the acidic nature of the original charcoal is responsible for catalysing this reaction.

It has been shown (Puri *et al.*, this *Journal*, 1957, **34**, 357) that the original charcoal by virtue of the presence of CO_2-complex is capable of undergoing surface ionisation in water, as represented below:

$$\mathbf{O}\text{-}CO_2 + H_2O \rightarrow \mathbf{O}\text{-}CO_3^{2-} \mid 2\,H^+.$$

It appears that surface hydrogen ions being directed towards the liquid phase react with sodium nitrite as:

$$\mathbf{O}\text{-}CO_3^{2-} \mid 2H^+ + 2\,NaNO_2 \rightarrow \mathbf{O}\text{-}CO_3^{2-} \mid 2\,Na^+ + 2\,HNO_2.$$

The resulting nitrous acid then undergoes oxidation to nitric acid by atmospheric oxygen contained in the bottle. The nitric acid supplies more hydrogen ions and thus the reaction, initiated by surface hydrogen ions of charcoal, continues further till in course of time the entire amount of nitrite ions is oxidised to nitrate ions provided that a sufficient amount of oxygen is available for the purpose.

The p_H values of charcoal, left after the reaction (determined after washing and drying), were found to increase from 2.85 to 7.60 after 2 hours and to 9.25 after 12 hours from the commencement of the reaction. This is evidently due to the replacement of the surface hydrogen ions by sodium ions, as represented by the equation given

above. and confirms the conclusion already arrived at regarding the mechanism of the reaction.

Charcoal containing acidic surface should also be able to bring about the oxidation of other oxidisable salts. The results obtained with sodium sulphite, potassium arsenite and potassium ferrocyanide are presented in Table III. The reason for smaller oxidations of sodium sulphite and potassium arsenite lies in the fact that sulphurous acid and arsenious acid formed in these reactions cannot be oxidised so easily.

TABLE III

Catalytic oxidation of sodium sulphite, potassium arsenite and potassium ferrocyanide by the original sample of charcoal.

	% Oxidation.				% Oxidation.		
Time of shaking.	Na sulphite.	K arsenite.	$K_4Fe(CN)_6$.	Time of shaking.	Na sulphite.	K arsenite.	$K_4Fe(CN)_6$.
2 hrs.	Nil	4.80	3.co	2 days	12.92	...	8.70
4	,,	5.48	4.21	3	14.60	8.22	11.13
8	1.12	6.38	5.70	5	...	10.27	...
12	2.81	6.85	6.26	10	...	13.29	...
24	7.39	...	6.94				

The oxidation of potassium ferrocyanide, represented by the equation,

$$2\,K_4[Fe(CN)_6] + H_2O + (O) \rightarrow 2\,K_3[Fe(CN)_6] + 2KOH,$$

should also be facilitated in the presence of original charcoal on account of its acid character and capacity to take up hydroxyl ions. The results in Table III show that this is actually the case. The evacuated samples of charcoal could not do so for obvious reasons.

If the mechanism proposed above for such reactions is correct, then the corresponding amounts of cations (Na^+ or K^+) should be fixed on the charcoal surface. This was verified by examining the charcoal left after the reaction. It was washed and dried in an electric oven maintained at 110°. A portion was then shaken with an excess of 0.1*N*-HCl. The amount of sodium (or potassium) chloride brought into solution was determined by evaporating the clear solution to complete dryness. The results obtained in a few experiments are shown in Table IV. It is evident that the amount of cation fixed on charcoal is almost exactly equivalent to the amount of the salt oxidised.

TABLE IV

Amounts of sodium nitrite and potassium ferrocyanide oxidised by 'original' sample and the cations fixed on charcoal surface.

	Sodium nitrite.		Potassium ferrocyanide.	
Time of shaking.	Amount oxidised.	Na^+ ions fixed on charcoal.	Amount oxidised.	K^+ ions fixed on charcoal.
2 hrs.	3.12 m.e./g.	2.97 m.e./g.	0.30 m.e./g.	...
4	4.25	4.33	0.42	0.45 m.e./g.
8	4.60	...	0.57	0.54
12	5.00	4.97	0.62	0.61
24	7.32	7.19	0.69	0.72
48	...	...	0.87	0.89
72	...	...	1.11	1.18

The surface hydrogen ions should also be able to bring about decomposition of salts like sodium thiosulphate and sodium bicarbonate, as represented below :

$$\mathbf{O}\text{-}CO_3^{2-} \vdots\ 2\,H^+ + Na_2S_2O_3 \longrightarrow \mathbf{O}\text{-}CO_3^{2-} \vdots\ 2\,Na^+ + H_2O + SO_2 + S$$

$$\mathbf{O}\text{-}CO_3^{2-} \vdots\ 2\,H^+ + 2\,NaHCO_3 \longrightarrow \mathbf{O}\text{-}CO_3^{2-} \vdots\ 2\,Na^+ + 2\,H_2O + 2\,CO_2$$

The data obtained by carrying out these reactions in closed bottles (Table V) show that this is actually the case. Evidently in these reactions no chain is set up and ultimately, when the surface hydrogen ions are replaced by alkali cations, the reactions should come to a stand-still, as has been found to be the case.

TABLE V

Catalytic decomposition of sodium thiosulphate and sodium bicarbonate by 'original' sample of sugar charcoal.

	% Decomposition.			% Decomposition.	
Time of shaking.	$Na_2S_2O_3$.	$NaHCO_3$.	Time of shaking.	$Na_2S_2O_3$.	$NaHCO_3$.
12 hrs.	1.98	22.73	3 days	8.51	51 13
24	3.50	38.64	4	8.76	...
48	4.52	44.32	6	11.25	60.52

It may be noted that although the sample evacuated at 750° contains an appreciable amount of oxygen (Table I), it is not capable of bringing about any of these reactions. This is evidently due to the fact that the chemisorbed oxygen contained in it is not present as an acid oxide. The view expressed by some early workers (vide Feigl, Brinkmann, Courty, *loc. cit.*) that the activity of charcoal to oxidise or decompose salt solutions may be due to the existence of a film of chemisorbed oxygen, needs modification in-as-much as that it is only due to that part of the chemisorbed oxygen which on high temperature evacuation is evolved as carbon dioxide.

DEPARTMENT OF CHEMISTRY,
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STUDIES IN CATALYTIC REACTIONS OF CHARCOAL. PART II. CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE

BALWANT RAI PURI, LEKH RAJ SHARMA AND D. D. SINGH

The catalytic decomposition of hydrogen peroxide solutions of different concentrations by sugar charcoal, original as well as degassed at 750° and at 1200°, has been studied in some details. The activity is found to be minimum in the case of the original sample and maximum in the case of the sample degassed at 1200°. The difference in the activity of the samples, prepared from the same material, can be attributed to the nature of their surface, acidic in the former and alkaline in the latter. The degassed sample chemisorbs an appreciable amount of oxygen in the course of the reation, leading to the formation of a surface-oxygen complex, capable of evolving CO_2 on high temperature evacuation. This complex renders the charcoal suface acidic and considerably lowers its activity for the reaction. A reasonable mechanism for the reaction has been suggested.

It is well known that hydrogen peroxide undergoes catalytic decomposition at the surfaces of dispersed solids. It is generally believed that large surface of these substances is responsible for their catalytic activity. Activated charcoal is also known to be an effective catalyst for the decomposition of hydrogen peroxide (Firth and Watson, *J. Chem. Soc.*, 1923, **123**, 1750 ; *Trans. Faraday Soc.*, 1924, **20**, 370 ; *J. Phys. Chem.*, 1925, **29**, 987 ; Skumburdis, *Kolloid Z.*, 1931, **55**, 156 ; King, *J. Chem. Soc.*, 1936, 1688). King (*loc. cit.*) and Larsen and Walton (*J. Phys. Chem.*, 1940, **44**, 476) have shown that the catalytic activity of charcoal depends upon the temperature of its activation, being maximum at 850° and minimum at 400°. Since the samples activated at 850° and 400° differ markedly in their p_H values (King, *J. Chem. Soc.*, 1935, 889) as well as acid-base adsorption capacity (Puri *et al.*, *Ind. Eng. Chem.*, 1958, **50**, 1071), it appears that the nature of the surface rather than its magnitude plays an important role in bringing about the reaction. The perusal of the literature shows that the mechanism of this reaction is not properly understood and several conflicting views have been put forward, amongst others by King (*loc. cit.*, 1936), Brinkmann (*Angew. Chem.*, 1949, **61**, 373 ; *Kolloid Z.*, 1951, **123**, 116) and Garten and Weiss (*Aust. J. Appl. Sci.*, 1956, **7**, 148).

EXPERIMENTAL

Charcoal samples.—Three samples of sugar charcoal, viz., (*i*) original, (*ii*) degassed at 750° and (*iii*) degassed at 1200°, as described in Part I (this *issue*, p. 765), were used in these experiments as well. Their surface areas, as calculated from water adsorption isotherms, were found to be 480, 491 and 486 sq. m/g. respectively.

Procedure.—The charcoal sample (1 g. portion each) was mixed with 100 c.c. of hydrogen peroxide solutions of different concentrations and the suspension shaken mechanically for 24 hours after which an aliquot of the clear supernatant liquid was titrated against a standard potassium permanganate solution. A blank was also run simultaneously in every case.

The results of decomposition of hydrogen peroxide solutions of different concentrations by the various samples of sugar charcoal are recorded in Table I.

TABLE I

Catalytic decomposition of H_2O_2 solns. of diff. conc. by the various samples of sugar charcoal.

Conc. of soln.	H_2O_2 added.	Amount decomp. (Blank).	H_2O_2 decomposed in the presence of charcoal samples. Original.	Degassed at 750°.	Degassed at 1200°.
0.10 *N*	10.0 m.e.	0.50 m.e.	0.50 m.e.	2.15 m.e.	5.00 m.e.
0.50	50.0	1.80	1.90	3.50	9.40
0.75	75.0	2.01	2.00	3.65	10.50
1.00	100.0	2.60	2.75	4.50	11 15
1.50	150.0	2.83	2.90	6.80	12.20
1.71	171.0	3.00	3.21	8.10	17.00
2 40	240.0	5.00	5.50	9.00	21.50
2.81	281.0	6.50	7.10	9.65	22.50
3.54	354.0	7.50	7.90	10.50	23 82
4.00	400.0	8.50	9.01	13.65	25.00

DISCUSSION

It is seen that the original sample has very little catalytic activity, the amount decomposed being only slightly larger than that decomposed in the absence of any foreign material. The evacuated samples, on the other hand, bring about the reaction to appreciable extents, the magnitude increasing with increase in the concentration of the peroxide solution.

Now since the original sample gave acid reactions in aqueous suspension (p_H 2.85) and those degassed at 750° and 1200° gave alkaline reactions (p_H 7.20 and 8.78 respectively), it appears that alkaline surface is far more conducive to catalytic decomposition of hydrogen peroxide than the acidic surface. Also, since all the three samples have nearly the same surface area, as already mentioned, it is evident that the nature, and not the magnitude of the surface, is of primary importance in bringing about this reaction.

Hydrogen peroxide, though an extremely weak acid, dissociates slightly as:

$$H_2O_2 \rightleftharpoons H^+ + OOH^-$$

and has a dissociation constant equal to 2.4×10^{-12}. It appears therefore quite probable that when hydrogen peroxide is brought in contact with the alkaline surface of the degassed charcoal, the first step in its decomposition lies in the adsorption of H^+ ions at the charcoal surface. This view receives support from the observations of Steenberg ("Adsorption and Exchange of Ions on Activated Charcoal", 1944, Almquist and Wiksells, Uppsala) that such charcoals can take up H^+ ions by primary adsorption from acid solution and that the acid anions are held next to hydrogen ions by electrostatic effect. Thus the OOH^- ions are held next to H^+ ions along the charcoal surface. Now the

OOH^- ions, being even less stable than the peroxide itself, decompose, liberating oxygen as represented below:

$$(C)\ H^+ : OOH^- \longrightarrow (C)\ H^+ : OH^- + (O)$$

The H^+ and OH^- ions may unite to form unionised water. This leaves the charcoal surface again in a position to take up more H^+ ions (unless it undergoes a fundamental change in its nature in the mean while, as discussed later, *vide infra*) and the dissociation and decomposition of hydrogen peroxide progress further.

It would be of interest to know the manner in which the oxygen given out by hydrogen peroxide in the presence of charcoal is disposed of. There are three possibilities: it might appear as free oxygen; it might oxidise some of the carbon to carbon dioxide and carbon monoxide, and finally it might be chemisorbed by the carbon, giving rise to surface-oxygen complexes. All the three possibilities were tested. For the first two, the gaseous mixture above the solution in each reaction bottle was sampled and analysed for its oxygen, carbon monoxide and carbon dioxide contents in the Orsat-Lunge gas analysis apparatus. The values were corrected for the amounts of these gases normally present in air, as determined by a similar analysis of the air in the room. For the third possibility, the charcoal left after the reaction was washed thoroughly with distilled water, dried and evacuated at 1200°. The gases evolved were analysed for CO, CO_2 and H_2O in the usual way. The results are shown in Tables II and III. It may be mentioned that no free carbon monoxide or carbon dioxide (in excess of the normal amount) was found above the reaction solution in any of the experiments, thus ruling out the second posibility altogether.

TABLE II

Decomposition of H_2O_2 by charcoal degassed at 750° and the account of oxygen rendered available.

[O_2 evolved as CO_2 on evacuating the treated samples at 1200° (II) = Nil].

Conc. of soln.	Amount decomposed with charcoal.	Free O_2 collected in the bottle. (I).	Total oxygen. (I+II).	p_H of aq. suspension of charcoal.
0.10 *N*	2.15 m.e.	2.20 m.e.	2.20 m.e.	7.20
0.50	3.50	3.44	3.44	7.21
0.75	3.65	3.70	3.70	6.99
1.00	4.50	4.40	4.40	7.18
1.50	6.80	6.71	6.71	7.05
1.71	8.10	7.99	7.99	7.10
2.40	9.00	8.89	8.89	6.98
2.81	9.65	9.72	9.72	7.13
3.54	10.50	10.43	10.43	6.97
4.00	13.65	13.40	13.40	7.23

TABLE III

Decomposition of H_2O_2 by charcoal degassed at 1200° and the account of oxygen rendered available.

Conc. of soln.	Amount decomposed with charcoal.	Free O_2 collected in the bottle. (I).	O_2 evolved as CO_2 on evacuating the treated samples at 1200°. (II).	Total oxygen. (I+II).	p_H of aq. suspension of charcoal.	Amount of H_2O_2 decomposed by charcoal sample already treated with 4*N*-H_2O_2.
0.10 *N*	5.00 m.e.	3.43 m.e.	1.51 m.e.	4.94 m.e.	8.78	.....
0.50	9.40	6.68	2.66	9.34	8.67	.....
0.75	10.50	6.97	3.48	10.45	7.80	.....
1.00	11.15	7.26	3.71	10.97	7.66	3.15 m.e.
1.50	12.00	7.88	4.00	11.88	7.12	3.41
1.71	17.00	11.02	5.98	17.00	6.78	.....
2.40	21.50	12.00	9.98	21.98	5.17	7.46
2.81	22.50	13.84	8.73	22.57	5.10	9.00
3.54	23.82	14.92	8.75	23.67	5.10	.....
4.00	25.00	16.38	9.15	25.53	5.12	11.15

It is evident that in the case of the reactions with the sample degassed at 750° (Table II), all the oxygen rendered available from the decomposition of hydrogen peroxide is evolved as elementary gas and that none of it is chemisorbed. There is consequently no change in the nature of the surface, the p_H value of charcoal remaining the same. However, in the reactions with the sample degassed at 1200° (Table III), some of the oxygen is evolved as elementary gas and the rest is chemisorbed by the charcoal. The latter is recovered entirely as CO_2 and not at all as CO or H_2O on subsequent evacuation at 1200°. It is interesting to note that the entire amount of oxygen resulting from the decomposition of hydrogen peroxide at each concentration is completely acounted for, partly as free oxygen and partly as chemisorbed oxygen. The latter, however, acquires a constant value after an appreciable decomposition has taken place and any oxygen rendered available thereafter is evolved as free gas. This shows incidentally that charcoal has only a limited capacity to chemisorb oxygen.

The presence of the oxygen complex capable of evolving CO_2 is known to render the charcoal surface acidic (Puri *et al.*, this *Journal*, 1957, **35**, 357). The p_H values of the aqueous suspensions of the residual charcoals left after the reaction were determined (Table III). It is seen that there is a progressive decrease in the p_H value of the charcoal, showing clearly that the charcoal undergoes distinct surface alterations (from basic to acidic character) in the course of the reaction.

Now, as acid surface cannot be so effective in bringing about the decomposition of hydrogen peroxide, the degassed charcoal should ultimately tend to lose its activity for this reaction. This was verified by working with the residual sample left after treatment with 4*N* solution of hydrogen peroxide and having p_H 5.12. The amounts of hydrogen

peroxide decomposed by it were now found to be extremely small (Table III, last column) and only slightly greater than the amounts decomposed in blank experiments (Table I).

In conclusion, it may be mentioned that the observations recorded in this paper can neither be explained satisfactorily by the reaction mechanism proposed by Brinkmann (*loc. cit.*) as it does not account for chemisorption of oxygen by charcoal and subsequent alterations in its surface characteristics nor by that, proposed by Garten and Weiss (*loc. cit.*) which, while providing for chemisorption of oxygen and surface alterations, cannot explain the removal of the entire amount of chemisorbed oxygen as carbon dioxide, which is actually the case. Moreover, the surface groups Postulated by them cannot remain intact on degassing carbons at 1200°. The mechanism proposed in the paper, on the other hand, appears to explain all the observed facts.

Department of Chemistry,
Panjab University,
Hoshiarpur.

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SULPHINATION. PART II. SULPHINATION OF SOME 7-HYDROXYCOUMARIN DERIVATIVES

By R. N. Usgaonkar and G. V. Jadhav*

Action of thionyl chloride on 4-methyl-6-propyl-7-hydroxycoumarin, 4-methyl-7-hydroxy-8-ethylcoumarin and methyl 4-methyl-7-hydroxy coumarin-6-carboxylate in presence of anhydrous aluminium chloride has now been studied. The first two coumarin derivatives react smoothly to give rise to respective sulphinic acids, while no reaction takes place on the last.

In continuation of our previous communication (this *Journal*, 1958, **35**, 251) the action of thionyl chloride on 4-methyl-6-propyl-7-hydroxycoumarin and 4-methyl-7-hydroxy-8-ethylcoumarin in presence of anhydrous aluminium chloride has been studied. Both the coumarins react smoothly, furnishing 4-methyl-6-propyl-7-hydroxycoumarin-8-sulphinic acid (I) and 4-methyl-7-hydroxy-8-ethylcoumarin-6-sulphinic acid (II) respectively, the sulphinic acid group entering into the position-8 in the former and the position-6 in the latter (the only free positions *ortho* to hydroxyl group in the respective coumarin derivatives). Both the sulphinic acids exhibit characteristic coloration with alcoholic ferric chloride, establishing the fact that $-SO_2H$ group is in position *ortho* to OH group.

The sulphonation of these coumarin derivatives with chlorosulphonic acid furnished the respective sulphonic acids which were found identical with those obtained by oxidation of the sulphinic acids (I) and (II), respectively, as judged by the mixed m.p. of the *s*-benzyl*iso*thiourea derivatives.

Attempts to sulphinate methyl 4-methyl-7-hydroxycoumarin-6-carboxylate with thionyl chloride met with failures.

Experimental

4-Methyl-6-propyl-7-hydroxycoumarin 8-sulphinic Acid (I)

Thionyl chloride (2.4 g.) was gradually added to an intimate mixture of powdered anhydrous aluminium chloride (4.2 g.) and 4-methyl-6-propyl-7-hydroxycoumarin (2 g.), cooled in ice and protected from moisture. It was left overnight at room temperature, and then decomposed by adding crushed ice and HCl. The resulting solution was kept in the refrigerator after scratching the walls of the container. The impure solid that separated after drying in vacuum was triturated with ammonia and then diluted with water. The insoluble residue contained, besides other byproducts, some amount of the ammonium salt of the sulphinic acid. The acid was recovered from it by extracting the residue with hot water and acidifying the extract.

The original ammoniacal filtrate was just acidified with HCl, when a dirty precipitate separated, which was filtered. To the clear filtrate more HCl was added, when sulphinic acid slowly separated. The dirty precipitate contained a little

* Present address: D.E. Society's Bombay College, Bombay-28.

amount of sulphinic acid as its ammonium salt. It was recovered by extracting it with hot water and acidifying the extract. The sulphinic acid was collected, washed well and dried in vacuum, m.p. 160-65° (decomp.), yield 1-1.5 g. It was crystallised from alcohol as white needles, m.p. 177-78° (decomp.). (Found: S, 11.79. $C_{13}H_{14}O_5S$ requires S, 11.34%).

It developed a blue coloration with alcoholic ferric chloride, and no fluorescence with alkali.

The *ammonium salt* was prepared by passing dry ammonia gas in an ice-cooled alcoholic solution of the sulphinic acid. It crystallised from alcohol (with few drops of water) in shining square plates, m.p. 214-15° (decomp.). (Found: N, 4.69. $C_{13}H_{17}O_5NS$ requires N, 4.68%).

s-*Benzylisothiourea derivative* was prepared by adding an aqueous solution of s-benzyl*iso*thiourea hydrochloride to the aqueous solution of the potassium salt. (Potassium salt was obtained by adding alcoholic potash dropwise to the alcoholic solution of sulphinic acid till yellow tinge appeared in the solution). It crystallised from alcohol in tiny needles, m.p. 155-56° (decomp.). (Found: N, 6.56. $C_{21}H_{24}O_6N_2S_2$ requires N, 6.25%).

4-*Methyl-6-propyl-7-hydroxycoumarin-8-sulphonic Acid*: (*i*) *Oxidation of Sulphinic Acid* (I).—Hydrogen peroxide (3 c.c. of 100 vol., diluted to 10 c.c.) was added to the potassium salt of the sulphinic acid (0.5 g.), suspended in water. It was left overnight at room temperature and then heated on a water-bath for half an hour and then cooled. The potassium salt of sulphonic acid slowly separated. It crystallised from water in shining needles.

s-*Benzylisothiourea derivative*, prepared from the above potassium salt, crystallised from dilute alcohol in thin needles, m.p. 174-75°. (Found: N, 6.18. $C_{21}H_{24}O_6N_2S_2$ requires N, 6.04%).

(*ii*) *Sulphonation with Chlorosulphonic Acid*.—Chlorosulphonic acid (1.3 c.c.) was gradually added to 4-methyl-6-propyl-7-hydroxycoumarin (1 g.) and the mixture (protected from moisture) was heated on a water-bath for 2½ hours, then cooled and poured over crushed ice. The solution was filtered and boiled to drive off hydrogen chloride. It was concentrated to a small bulk and then added to a small quantity of saturated solution of common salt, when sodium salt of sulphonic acid slowly separated. It was filtered, washed and dried.

s-*Benzylisothiourea derivative*, prepared from the above sodium salt, crystallised from dilute alcohol, m.p. and mixed m.p. with previous specimen, 174-75°.

4-*Methyl-6-propyl-7-hydroxycoumarin-8-ethylsulphone*.—A solution of potassium salt of sulphinic acid (I, 0.7 g.) in a mixture of alcohol (4 c.c.) and water (3 c.c.) was refluxed with ethyl iodide (10.8 c.c.) for 18 hours. The reaction mixture was filtered hot. From the filtrate the sulphone slowly crystallised out. The solid was washed with thiosulphate solution to remove iodine and then with water. It was crystallised from alcohol in white shining plates, m.p. 145-47°. (Found: S, 10.42. $C_{15}H_{18}O_5S$ requires S, 10.32 %).

4-Methyl-7-hydroxy-8-ethylcoumarin-6-sulphinic Acid (II)

Thionyl chloride (1.5 c.c.) was gradually added to an intimate mixture of powdered anhydrous aluminium chloride (4.4 g.) and 4-methyl-7-hydroxy-8-ethylcoumarin (2 g.) (Limaye and Ghate, *Rasayanam*, 1939, **6**, 171) and the reaction was allowed to proceed in the same way as before, and was worked up similarly.

The residue obtained after triturating the crude solid with ammonia was found to be mainly the unchanged coumarin. The solution was just acidified with HCl and the mud-like precipitate separating was removed, and to the clear filtrate more HCl was added, scratched and left in the refrigerator. The sulphinic acid, which slowly separated, was collected, washed with water and dried in vacuum, m.p. 150° (decomp.), yield 1-1.2 g. It was crystallised from dilute alcohol, m.p. 155° (decomp.). (Found : S, 11.97. $C_{12}H_{12}O_5S$ requires S, 11.94%).

It developed a violet coloration with alcoholic ferric chloride, and no fluorescence with alkali.

The *ammonium salt* was prepared and crystallised as before in shining needles, m.p. 204-205° (decomp.). (Found : S, 4.98. $C_{12}H_{13}O_5NS$ requires S, 4.91%).

s-*Benzylisothiourea derivative*, prepared as usual from the sulphinic acid (by first preparing the neutral solution of sodium salt of sulphinic acid), was crystallised from dilute alcohol in glistening needles, m.p. 190-92° (decomp.). (Found : N, 6.80. $C_{20}H_{22}O_5N_2S_2$ requires N, 6.45%).

4-Methyl-7-hydroxy-8-ethylcoumarin-6-sulphonic Acid : (*i*) *Oxidation of Sulphinic Acid* (II).—Hydrogen peroxide (3 c.c. of 100 vol. and 7 c.c. of water) was added to the solution of the sulphinic acid (0.5 g.) in sodium bicarbonate solution (5 c.c.). The reaction mixture was left aside at room temperature for some time and then heated on a water-bath for about an hour. It was cooled, just acidified with HCl and then filtered from any impurities. The solution was concentrated to a small bulk and poured in a saturated solution of common salt and cooled. The sodium salt of sulphonic acid slowly separated as a crystalline solid.

s-*Benzylisothiourea derivative*, prepared from the sodium salt, was crystallised from dilute alcohol in shining plates, m.p. 125-27°. (Found : N, 6.56. $C_{20}H_{22}O_6N_2S_2$ requires N, 6.22%).

(*ii*) *Sulphonation with Chlorosulphonic Acid.*—Chlorosulphonic acid (0.8 c.c.) was gradually added to 4-methyl-7-hydroxy-8-ethylcoumarin (1 g.) and the mixture, protected from moisture, was heated on a water-bath for 2 hours. It was cooled, well mixed with crushed ice and the resulting solution was filtered. The filtrate was boiled to drive off HCl, concentrated to a small bulk and added to a saturated solution of common salt and then kept in the refrigerator, when a white sodium salt separated. It was filtered, washed with alcohol and dried.

s-*Benzylisothiourea derivative*, prepared from the sodium salt, was crystallised from alcohol in shining plates, m.p. and mixed m.p. with the previous specimen, 125-27°.

4-Methyl-7-hydroxy-8-ethylcoumarin-6-ethylsulphone.—A solution of ammonium salt of the sulphinic acid (II, 0.5 g.) in a mixture of alcohol (8 c.c.) and water (4 c.c.) was refluxed with ethyl iodide (0.8 c.c.) for 18 hours. The solution was filtered hot, and concentated. The crystalline solid separating was washed with a thiosulphate solution to remove iodine and then with a little alcohol. It was crystallised from alcohol in white needles, m.p. 162-63°. (Found : S, 10.4. $C_{14}H_{16}O_5S$ requires S, 10.8 %).

ORGANIC CHEMISTRY LABORATORIES,
THE INSTITUTE OF SCIENCE,
BOMBAY.

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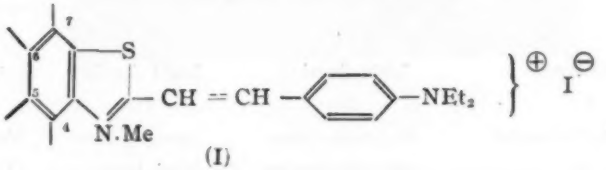
SYNTHESIS OF CYANINE DYES BY THE CONDENSATION OF *p*-DIETHYLAMINOBENZALDEHYDE WITH APPROPRIATE HETEROCYCLIC COMPOUNDS. PART VIII

By M. Q. Doja and J. C. Banerji

Four new dyes have been prepared by condensing *p*-diethylaminobenzaldehyde with the methiodides of 2 : 4-dimethyl-, 2 : 5-dimethyl-, 2 : 7-dimethyl- and 2-methyl-6-iodo-benzthiazole, and ther optical and other properties examined. Results of previous communications have been collected andi it has been shown that the substitution at the 4-position of the benzthiazole nucleus affords maximum extra-sensitisation. It has also been shown that the substituents at the 4-position fall in the order: EtO->Me->Cl, Br->MeO->I- with respect to extra-sensitisation.

The present series of investigations were undertaken with a view to studying the effect of substitution on the extra-sensitisation of the *p*-diethylaminostyryl type of cyanine dyes containing a benzthiazole nucleus. For this purpose various substituents have been introduced into the 6-position of *p*-diethylaminostyrylbenzthiazole methiodide (I), and at the same time one particular substituent has been introduced at all of the four positions available for substitution in the benzthiazole nucleus. The sensitisation spectra of the dyes, thus obtained, have been compared with those of the unsubstituted dye.

Some of the results of these investigations have already been reported (Doja and Banerji, this *Journal*, 1946, **23**, 217; 1949, **26**, 374; 1951, **28**, 7). For the sake of completeness, four new dyes have been prepared by condensing *p*-diethylaminobenzaldehyde with the methiodides of 2 : 4-, 2 : 5- and 2 : 7-dimethylbenzthiazoles and of 6-iodobenzthiazole in absolute ethanol, using piperidine as a catalyst. The dyes may be represented by the general expression (I) (substitutents not shown):



(I)

which represents the resonance hybrid between the two extremes, in one of which the heterocyclic and in the other the exocyclic nitrogen has the positive charge.

The required methiodides were prepared in all cases by the prolonged heating of the respective base with methyl iodide in a sealed tube on the water-bath.

The rectified spirit solutions of the dyes are all magenta-coloured, the colour being reversibly discharged by the addition of mineral acids, as is the characteristic of

all cyanine dyes. The resistance to decolorisation was determined by titrating 2 c.c. of 1/2000 solution of the dyes in rectified spirit against $N/100$-HCl. The results are shown in Table I.

TABLE I

Dye.	Colour and shape of the crystals.	Reflex.	Pleochroism. Colour of light at one position of polariser.	Pleochroism. Colour of light at ⊥ to the polariser.	$N/100$-HCl reqd.	$\lambda_{max.}$	Frequency of max. (10^{10}).
C	Dark thin elongated needles	Weak yellowish green	Glass like	Nearly opaque	16.0 c.c.	4960 Å	60484
F	Moss-green	Green	Nearly colorless	Bottle-green	19.5	5000	60000
O	Shining dark grey needles	Pinkish yellow	Light green	Brownish green	17.5	5300	56603
H	Dull brinjal coloured needles	Nil	Slate grey	Colorless	18.0	5100	58821

The dyes produce various shades on cotton, silk and wool which, however, fade on washing and on exposure to sunlight. The shades obtained are shown in Table II.

TABLE II

Dye.	Colour developed on		
	Cotton.	Silk.	Wool.
C	Mauve	Mauve	Dull pink
F	Purple	Light magenta	Light magenta
O	Mauve	Violet-red	Bluish red
H	Bluish red	Violet-red	Pink

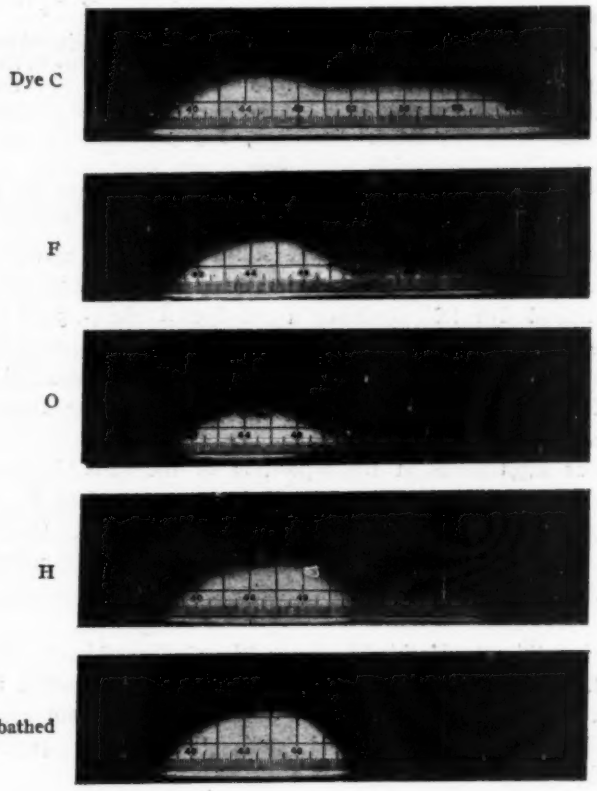
The fluorescence of weak alcoholic solutions (1/50,000) of the dyes (cf. Doja, this *Journal*, 1940, **17**, 348) are shown in Table III.

TABLE III

Wallace colour filter No.	Colour of the fluorescent beam seen at right angle to the incident beam passing through soln. of the dyes			
	C.	F.	O.	H.
1	Weak red	Light absorbed	Light absorbed	Light absorbed
2	Do	Do	Do	Do
3	Light absorbed	Brownish yellow	Orange-yellow	Weak orange-yellow
4	Do	Brownish orange	Weak brown	Light brown
5	Dull yellow	Lemon-yellow	Orange-yellow	Yellowish brown
6	Weak rose-red	Dull yellow	Carrot-yellow	Dirty yellow
7	Yellow	Greenish yellow	Light absorbed	Greenish yellow
8	Yellow	Orange-brown	Do	Orange-brown
9	Orange-yellow	Orange-yellow	Orange-yellow	Orange-yellow
10	Do	Brownish yellow	Pink-yellow	Brownish yellow

Some of the other properties of the dyes are also recorded in Table I. The sensitisation spectra are shown in Fig. 1. For the sake of comparison, the sensitisation spectrum of an unbathed process plate is appended in Fig. 1.

FIG. 1



Acetic acid solutions of the dyes deepened in intensity on warming and the original intensity was regained on cooling, the effect being more pronounced in aqueous acetic acid solutions (cf. Doja and Banerji, *loc. cit.*).

The sensitisation spectra of some of the dyes reported previously (Doja and Banerji, *loc. cit.*) were retaken with a slight improvement in the technique. The results obtained together with those of the dyes now prepared are shown in Table IV.

TABLE IV

Dye.	Nature of substitution.	Extra-sensitisation. Range.	Maxima.	Remarks.
X	Unsubstituted	5200-6350 Å	Gradual decay	Doja and Banerji (this *Journal*, 1946, **23**, 217). Retaken.
C	4-Methyl	4920-6840	5440, 6020 Å	
F	5-Methyl	5100-6280	5600, 6000	
S	6-Methyl	4800-6750	5620	Doja and Banerji (*ibid.*, 1949, **26**, 374). Retaken.
O	7-Methyl	5000-6620	5600, 6000	
L	6-Methoxy	4860-6520	Gradual decay	Doja and Banerji (*ibid.*, 1951, **28**, 7). Retaken.
M	6-Ethoxy	5000-6760	5800	Do
N	6-Chloro	5000-6560	5500	Do
P	6-Bromo	5180-6560	5400, 5800, 6300	Do
H	6-Iodo	5160-6260	6000	
T	4 : 6-Dimethyl	5000-6540	5600	Doja and Banerji (*loc. cit.*, p. 374). Retaken.

It will be seen from Table IV that the substitution of a methyl group in the benzthiazole nucleus of the parent dye affects the sensitisation profoundly. Thus, while the unsubstituted dye (X) sensitises up to 6350 Å, the 4-, 5-, 6- and 7-methyl-substituted dyes sensitise up to 6840, 6280, 6750 and 6620 Å respectively. Arranged in order of extra-sensitisation, the available positions for substitution fall in the order: 4-Me>6-Me>7-Me>5-Me. The 5-methyl dye is a weaker sensitiser than the unsubstituted parent dye.

Of the various substituents at the 6-position of the benzthiazole nucleus, the ethoxy group imparts the greatest extra-sensitisation (up to 6760 Å), the different substituents falling in the order: EtO->Me- >Cl-, Br->MeO > I. Curiously enough the 4 :6-dimethyl dye is a weaker sensitiser than either of the singly methyl-substituted 4-methyl or 6-methyl dye.

EXPERIMENTAL

2 :4-*Dimethylbenzthiazole Methiodide*.—2 :4-Dimethylbenzthiazole (Kiprianov and Sitsch, *Trav. Inst. Chem.*, Charkov, 1936, **2**, 25) and methyl iodide (1 :1.5 molar) were heated for 24 hours in a sealed tube in a water-bath and the salt was recrystallised from absolute ethanol, m.p. 223°, yield 77%. (Found: I, 41.72. $C_{10}H_{12}NIS$ requires I, 41.64%).

2-p-*Diethylaminostyryl-4-methylbenzthiazole Methiodide* (Dye C).—The above methiodide (0.3 g.), *p*-diethylaminobenzaldehyde (0.18 g.), absolute ethanol (5 c.c.) and piperidine (2 drops) were refluxed for 4 hours. The dye (19%) separated on cooling and it was recrystallised from methanol as indigo-blue slender needles, m.p. 210°. (Found: N, 5.98; I, 27.30. $C_{21}H_{23}N_2IS$ requires N, 6.04 ; I, 27.37%).

2 :5-*Dimethylbenzthiazole Methiodide*.—2 :5-Dimethylbenzthinzole (Banerji, this *Journal*, 1955, **32**, 135) and methyl iodide (1 :1.5 molar) were heated in a sealed tube for 24 hours on a water-bath and the salt was recrystallised from hot water as colorless needles, m.p. 211°, yield 81%. (Found: I, 41.57. $C_{10}H_{12}NIS$ requires I, 41.64%).

2-p-*Diethylaminostyryl-5-methylbenzthiazole Methiodide* (Dye F).—On refluxing the above methiodide (0.6 g.), *p*-diethylaminobenzaldehde (0.36 g.), absolute ethanol (5 c.c.) and piperidine (2 drops) for 14 hours, the dye separated (45%) as greenish golden yellow platelets and it was recrystallised from methanol, m.p. 218°. (Found: N, 6.18; I, 27.21. $C_{21}H_{25}N_2IS$ requires N, 6.04; I, 27.37%).

2:7-*Dimethylbenzthiazole Methiodide*.—2:7-Dimethylbenzthiazole (Banerji, *loc. cit.*) and methyl iodide (1:1.5 molar) were heated in a sealed tube in a water-bath for 24 hours and the salt was recrystallised from hot water as faint pink, elongated needles, m.p. 240°, yield 88%. (Found: I, 41.48. $C_{10}H_{12}NIS$ requires I, 41.64%).

2-p-*Diethylaminostyryl-7-methylbenzthiazole Methiodide* (Dye O).—The above methiodide (0.6 g.), *p*-diethylaminobenzaldehyde (0.36 g.), absolute ethanol (10 c.c.) and piperidine (2 drops) were refluxed for half an hour. The dye began to separate even while the solution was boiling. On cooling, the dye (63%) was obtained as woolly needle clusters and was recrystallised from methanol, m.p. 227°. (Found: N, 6.12; I, 26.96. $C_{21}H_{25}N_2IS$ requires N, 6.04; I, 27.37%).

p-*Iodothioacetanilide*.—*p*-Iodoacetanilide (20 g.) and phosphorus pentasulphide (12 g.) were intimately mixed and the mixture was treated with boiling xylene (50 c.c.) for a short time. The hot xylene extract, decanted from the tarry residue, deposited on cooling *p*-iodothioacetanilide (4 g.) as buff-coloured needles, m.p. 147-48°. Worral (*J. Amer. Chem. Soc.*, 1924, **46**, 2837), who prepared it from substituted aromatic mustard oils, reported m.p. 149°. The crude product was used in the subsequent preparation without further purification.

2-*Methyl-6-iodobenzthiazole*.—To a filtered solution of *p*-iodothioacetanilide (4 g.) in 2*N*-NaOH solution (100 c c.) a 20% potassium ferricyanide solution (50 c.c.) was added and the mixture allowed to stand overnight. The base settled down as a thick viscous mass. The aqueous layer was removed and the residue was washed repeatedly with water. The residue on recrystallisation from hot aqueous ethanol (bone charcoal) furnished the thiazole as long white needles (25%), m.p. 140-41°. This compound was prepared by Kiprianov, Ushenko and Sitsch (*J. Gen. Chem. USSR.*, 1945, **15**, 200) by Sandmeyer's reaction on 6-amino-2-methylbenzthiazole, m.p. 142°.

2-*Methyl-6-iodobenzthiazole Methiodide*.—On heating the above base with methyl iodide (1:1.5 molar) in a sealed tube in a water-bath for 24 hours, the salt was obtained and was recrystallised from hot water (bone charcoal) as stout colorless needles, (79%), m.p. 239°. (Found: I, 60.1. $C_9H_9NI_2S$ requires I, 60.9%).

2-p-*Diethylaminostyryl-6-iodobenzthiazole Methiodide* (Dye H).—On refluxing a mixture of the above methiodide (0.45 g.), *p*-diethylaminobenzaldehyde (0.2 g.), absolute alcohol (5 c.c.) and piperidine (2 drops) for 2 hours, the dye was obtained (33%) and was recrystallised from methanol as greenish blue needles, m.p. 253-54°. (Found: N, 4.91; I, 43.87. $C_{20}H_{22}N_2I_2S$ requires N, 4.86; I, 44.09%).

The authors wish to thank Professor L.M. Chatterjee, Science College, Patna, for his kind help in recording the absorption and sensitisation spectra of the dyes.

CHEMICAL LABORATORIES,
B.N. COLLEGE AND SCIENCE COLLEGE, PATNA.

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POTENTIOMETRIC STUDY OF THE REACTION BETWEEN DICHROMATE AND HYDROGEN PEROXIDE. ACTION OF MANGANOUS SULPHATE

By K. Chatterjee and B. P. Gyani

Dichromate is quantitatively reduced by H_2O_2 to give chromic ions if the acid concentration is properly adjusted (8*N* to *N*/2-H_2SO_4 or 2*N* to *N*-HCl). Four moles of H_2O_2 per mole of dichromate are required, which can be explained on the assumption that the dichromate (oxidation state Cr_2O_6) first acquires an unstable higher oxidation state, Cr_2O_{10}, from which oxygen is evolved and Cr_2O_3 (*i. e.*, chromic ions in acid solution) is left behind. When the acid concentrations are less, somewhat more than 4 moles of H_2O_2 are required, indicating either a higher oxidation state, Cr_2O_{11}, or self-decomposition of the peroxide. When manganous sulphate in excess is added before the peroxide is run in (10*N* to 2*N*-H_2SO_4), three moles of peroxide are required, perhaps in accordance with the mechanism, $Cr_2O_6 + 6MnO \rightarrow Cr_2O_3 + 3Mn_2O_3$; $3Mn_2O_3 + 3H_2O_2 \rightarrow 3Mn_3O_4 + 3H_2O$; $3Mn_2O_4 \rightarrow 6MnO + 3O_2$, so that the action of manganous ions is only catalytic.

A number of potentiometric methods of analysing hydrogen peroxide solution has been described, a critical review of which is given by Reichert *et al.* (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 194). It appears that a potentiometric method of estimation of H_2O_2 with $K_2Cr_2O_7$ has not yet been attempted.

When treated with hydrogen peroxide, acidic solutions of chromates produce the well-known blue perchromic acid (Sidgwick, "The Chemical Elements and their Compounds", Oxford University Press, 1950, p. 1006), which quickly decomposes in aqueous solutions at ordinary temperatures, producing an equivalent amount of Cr^{3+}. The reduction of $Cr_2O_7^{2-}$ by H_2O_2 is complicated by this fact, and there has been considerable controversy regarding the formation and composition of the blue perchromic acid. Carnot (*Compt. rend.*, 1888, **107**, 948, 997, 107) found that the reduction of $Cr_2O_7^{2-}$ by H_2O_2 was quantitative. Berthelot (*ibid.*, 1889, **108**, 24, 157, 477) considered that due to the intermediate formation of unstable perchromic acids, the amount of H_2O_2 required to reduce the dichromate was likely to vary with the mode of admixture, the presence of particular acids, temperature and concentration. He found that very dilute dichromate in HCl required four moles of H_2O_2 per mole of $K_2Cr_2O_7$ and represented the reaction as

$$2HCrO_4 + 4H_2O_2 + 6HCl = Cr_2Cl_6 + 4O_2 + 8H_2O.$$

He also found that dichromate in sulphuric acid required 3 moles H_2O_2 when the latter was added to the former, but 5 moles, when the process was reversed. For 3 moles of H_2O_2 consumed per mole of dichromate, the reaction was set down as

$$2CrO_3 + 3H_2O_2 + 3H_2SO_4 = Cr_2(SO_4)_3 + 6H_2O + 3O_2.$$

For 5 moles, it was represented in two stages :

$$2CrO_3 + H_2O_2 = Cr_2O_7 + H_2O,$$

followed by

$$Cr_2O_7 + 4H_2O_2 = Cr_2O_9 + 4H_2O + 4O_2.$$

Cr_2O_7 was here assumed to be the anhydride of the intermediate perchromic acid, which he considered to be $HCrO_4$.

According to Riesenfeld *et al.* (*Ber.*, 1905, **38**, 3380, 3578) only three moles of H_2O_2 per two moles of CrO_3 are required, irrespective of the mode of admixture. They considered that the reduction took place with the formation of an intermediate,

$$Cr_2O_9, 2CrO_3 + 3H_2O_2 = 2Cr_2O_9 + 3H_2O,$$

followed by

$$Cr_2O_9 = Cr_2O_3 + 3O_2.$$

The results of Schwarz and Giese (*Ber.*, 1932, **65**, 871) suggest that the anhydride of the intermediate perchromic acid is neither Cr_2O_7 nor Cr_2O_9, but CrO_5. This formula requires four moles of H_2O_2 per two moles of CrO_3 for the reduction, as is shown later.

Rai (this *Journal*, 1957, **35**, 193) assumes that the formation of the ethereal blue peroxychromic acid may be due to the combination of $Cr_2O_{10}^{2-}$ and Cr^{3+}, the latter generated by simultaneous reduction by H_2O_2. The mechanism suggested by him would again require three moles of H_2O_2 per mole of dichromate reduced, the intermediate compound being $Cr_2(Cr_2O_{10})_3$. Recent investigations by Glasner and Steinberg (*J. Chem. Soc.*, 1957, 2559) indicate that the basic formula of the intermediate compound is CrO_5. This agrees with the results of Schwarz and Giese (*loc. cit.*) and Evans (*J. Chem. Soc.*, 1957, 4013) who find that the predominant equilibrium in an aqueous solution is

$$HCrO_4^- + 2H_2O_2 + H^+ \rightleftharpoons CrO_5 + 3H_2O.$$

The formula CrO_5 for the blue perchromic acid requires four moles of H_2O_2 per two moles CrO_3,

$$2CrO_3 + 4H_2O_2 = 2CrO_5 + 4H_2O.$$

This is followed by

$$2CrO_5 = Cr_2O_3 + 3.5O_2.$$

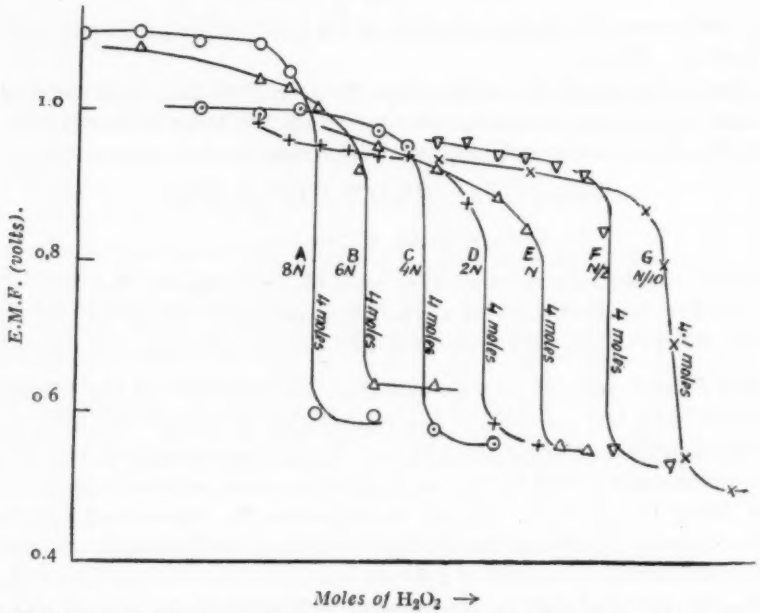
A potentiometric titration of dichromate with H_2O_2 promised to be of much interest in this context and the present work was taken up with a view to obtaining a clearer picture of the reduction of dichromate by peroxide. The role of an excess of $MnSO_4$, previously noted (this *Journal*, 1957, **35**, 721), has been further studied.

EXPERIMENTAL

Titrations were all performed at room temperature ($24° \pm 2°$) using the potentiometric arrangements described earlier (this *Journal*, 1955, **32**, 313). The reaction mixtures, prepared as follows, were taken in the titration cell and kept stirred with a magnetic stirrer, half-molar peroxide being added from a burette: sulphuric acid mixtures (A) $8N$, (B) $6N$, (C) $4N$, (D) $2N$, (E) N, (F) $N/2$ and (G) $N/10$; hydrochloric acid mixtures (A) $2N$, (B) N, (C) $N/2$ and (D) $N/10$. The concentration of dichromate was $0.005M$ in all these mixtures and 100 c.c. was taken for a titration.

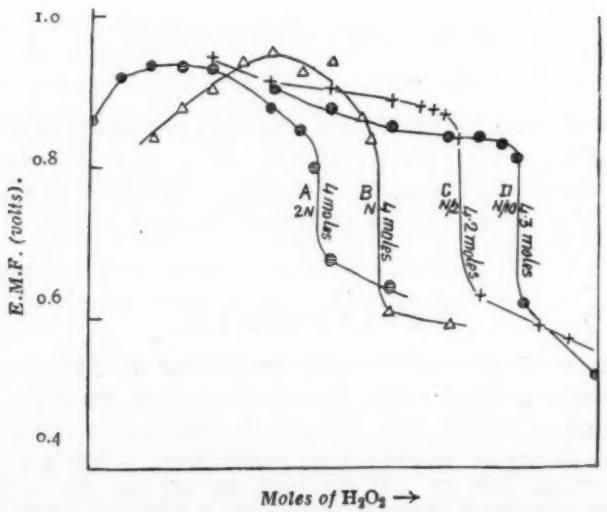
Higher concentrations of HCl were avoided to eliminate the possibility of evolution of Cl_2.

FIG. 1



A blackish precipitate appeared on addition of H_2O_2, which soon redissolved, exhibiting a greenish tinge to the solution (orange due to dichromate). At the point

FIG. 2



of inflection, the colour changed over sharply from greenish yellow to blue, indicating complete reduction of Cr^{3+}. The black precipitate took long to dissolve when the

acid concentration was less than normal. The potentials were fairly steady after fifteen minutes of constant stirring. The potential drop at the equivalence point was 250-400 mv. The actual graphs are reproduced in Figs. 1 and 2 for sulphuric acid and hydrochloric acid mixtures respectively, the letters corresponding to the individual mixtures. The inflection occurs at 4 moles of H_2O_2 in all H_2SO_4 mixtures except (G) where it is about 4.1. For HCl mixtures also, the H_2O_2 requirement is increased from 4 moles (A, B) to larger values when acid concentration is reduced (C=4.2, D=4.3).

To study the effect of an excess of $MnSO_4$, a series of mixtures, 0.005*M*-$K_2Cr_2O_7$ and 0.3*M*-$MnSO_4$, were prepared with decreasing H_2SO_4 concentrations: (A) 10*N*, (B) 8*N*, (C) 6*N*, (D) 4*N*, (E) 2*N* and (F) *N*. The corresponding graphs appear in Fig. 3.

On mixing the dichromate and manganous sulphate solutions, a deep cherry-red colour appeared, indicating oxidation of Mn^{2+} to Mn^{3+}. To complete the oxidation, the reaction mixture was stored in the dark for several hours before the H_2O_2 was run in. The depth of the red colour decreased as the peroxide was added, and the colour changed over to greenish blue at the equivalence point (not sharp). Ten minutes of stirring was necessary for a steady potential, and the potential drop at the equivalence point was about 400 mv. The peroxide requirement per mole of $K_2Cr_2O_7$ was three in A to E, but higher when acid concentration was below 2*N* (3.5 moles H_2O_2 in F).

Discussion

An understanding of the reactions taking place is simplified if we ignore the identity of the various oxides and acids formed and concentrate on the correct oxidation states only of chromium and manganese. We have to adopt the assumption that in general all the H_2O_2 is first consumed in producing a higher oxidation state of Cr or Mn, which being unstable decomposes to produce oxygen and lower oxidation states of the metals. The oxidation state of the dichromate may conveniently be taken as Cr_2O_6. For four moles of H_2O_2 consumed (Fig. 1, A to F; Fig. 2, A & B) the steps may be written,

$$Cr_2O_6 + 4H_2O_2 \longrightarrow Cr_2O_{10} + 4H_2O$$

$$Cr_2O_{10} \longrightarrow Cr_2O_3 + 3.5O_2.$$

At smaller acid concentrations (Fig. 1, G ; Fig. 2, C, D) a little more than four moles of H_2O_2 is required. This may hardly be explained on the basis that self-decomposition of the peroxide may set in under the changed conditions of the experiment. Alternatively, a small quantity of Cr_2O_6 may attain a still higher oxidation state, Cr_2O_{11}:

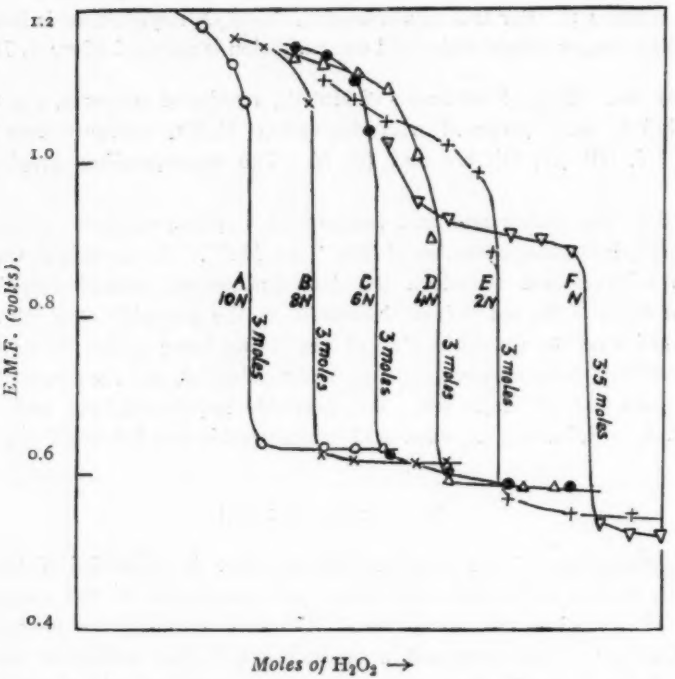
$$Cr_2O_6 + 5H_2O_2 \longrightarrow Cr_2O_{11} + 5H_2O$$

$$Cr_2O_{11} \longrightarrow Cr_2O_3 + 4O_2.$$

When an excess of $MnSO_4$ is present, only three moles of the peroxide are consumed. The colour changes accompanying the reduction indicate the following reactions:

$$Cr_2O_6 + 6MnO \longrightarrow 3Mn_2O_3 + Cr_2O_3$$
$$3Mn_2O_3 + 3H_2O_2 \longrightarrow 3Mn_2O_4 + 3H_2O$$
$$3Mn_2O_4 \longrightarrow 6MnO + 3O_2.$$

FIG. 3



When a lesser quantity of acid is present (Fig. 3, F), the requirement of peroxide may be increased to 3.5 moles or more. Since the reaction,

$$3Mn_2O_3 + 4H_2O_2 \longrightarrow Mn_6O_{13} + 4H_2O,$$

appears to be unlikely, it is probable that a little of the Cr_2O_6 escapes reduction by $MnSO_4$ and reacts as if this salt were absent. The intermediate oxidation states discussed here are all unstable. Their identifications are therefore no simple matter. For the same reason it is hardly possible to understand these reactions on the basis of the corresponding redox potentials. We would show particular reluctance to the identification of Mn_2O_4 as manganese dioxide as this substance is a powerful catalyst for the decomposition of H_2O_2 in solution. As a first step towards confirmation of these mechanisms, it is necessary to measure the volume of oxygen evolved. This matter is receiving our attention.

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CHEMISTRY DEPARTMENT,
B. N COLLEGE, PATNA 4.

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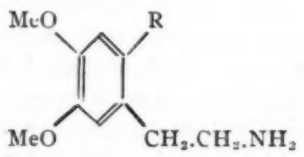
SEARCH FOR NEW AMOEBACIDES. PART III

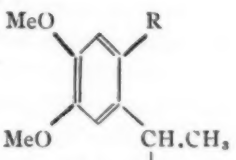
By K. L. Pathak and B. Pathak

Some β-(2-alkyl-4 :5-dimethylphenyl)-ethylamines and α-(2-alkyl-4 : 5-dimethoxyphenyl)-ethylamines having n-C_8H_{17}, n-$C_{10}H_{21}$ and n-$C_{12}H_{25}$ alkyl substitution have been synthesised.

Syntheses of some β-(2-alkyl-4 : 5 dimethoxyphenyl)-ethylamines (I) and α-(2-alkyl-4 : 5-dimethoxyphenyl)-ethylamines (II) have been described in previous papers (this *Journal*, 1957, **34**, 611, 768). Amoebacidal activity of some of these compounds has been described by Kaushiva (*J. Sci. Ind. Res.*, 1957, **16C**, 224). In view of the high *in vitro* activity of the compounds (I and II : R = n-hexyl) it has been considered worthwhile to prepare and examine the activity of compounds of both the series having higher alkyl chains. A few compounds of the type (I) were previously prepared by the Hofmann reaction on the appropriate amides, and it was mentioned in Part I (*loc. cit.*, p. 611) that the yield of the amine decreased with the increase of chain length.



(I)



(II)

We have failed to prepare the compound (I : R = n-octyl) by the Hofmann reaction on the appropriate amide. These amines have been prepared by reduction of the β-nitrostyrenes with $LiAlH_4$. Yields are poor and vary from 25 to 40% of the theoretical. Appropriate β-nitrostyrenes have been prepared according to the procedure of Lange and Hambourger (*J. Amer. Chem. Soc.*, 1931, **53**, 3865).

It has also been observed that the yield of 2-alkyl-4 : 5-dimethoxy-acetophenone decreases enormously with the increase of chain length.

*Experimental

3 : 4-*Dimethoxyphenyl*-n-*heptyl Ketone*.—A mixture of veratrole (48 g.), n-caprylic acid chloride (48 g.), dry CS_2 (400 c.c.) and powdered $ZnCl_2$ (anhyd., 100 g.) was refluxed on a water-bath for 6 hours and then left overnight. CS_2 was removed by distillation and the residue was decomposed by water and then boiled for half an hour with HCl. The mixture was cooled and extracted with benzene. The benzene solution yielded the ketone (42 g.), b.p. 165-68°/4 mm.

The 2 : 4-*dinitrophenylhydrazone* was crystallised from alcohol in red needles, m.p. 130-31°. (Found : N, 12.8. $C_{22}H_{28}O_6N_4$ requires N, 12.61%).

* Melting and boiling points are uncorrected.

3 : 4-*Dimethoxyphenyl*-n-*nonyl ketone* was crystallised from alcohol in white needles, b.p. 198-200°/2 mm, m.p. 62°, yield 43%.

The 2 : 4-*dinitrophenylhydrzone* was crystallised from alcohol in red needles, m.p. 90-91°. (Found : N, 12.1. $C_{24}H_{32}O_6N_4$ requires N, 11.87%).

3 : 4-*Dimethoxyphenyl* - n-*undecyl ketone* was crystallised from alcohol in white needles, b.p. 200°/1 mm, m.p. 70 71°, yield 55%.

The 2 : 4-*dinitrophenylhydarazone* was crystallised from alcohol in red needles, m.p. 80-81°. (Found : N, 11.3. $C_{26}H_{36}O_6N_4$ requires N, 11.2%).

1-n-*Octyl*-3 : 4-*dimethoxybenzene*.—3 : 4-Dimethoxyphenyl-*n*-heptyl ketone (27 g.) in alcohol (30 c.c.) was reduced with amalgamated zinc (90 g.) and HCl. After reduction was over (about 8 hours), the product was diluted with water and the separated oil was extracted with benzene. Benzene was distilled off and the residual oil was distilled in vacuum, b.p. 148-50°/0.4 mm, yield 16 g. (Found : C, 76.6; H, 10.5. $C_{16}H_{26}O_2$ requires C, 76.81 ; H, 10.40%).

1-n-*Decyl*-3 : 4-*dimethoxybenzene*.—B.p. 171-72°/2 mm, yield 80%. (Found : C, 77.4 ; H, 10.6. $C_{18}H_{30}O_2$ requires C, 77.7 ; H, 10.79%).

1-n-*Dodecyl*-3 : 4-*dimethoxybenzene*.—B.p. 180°/0.5 mm or 195°/2 mm, yield 59%. (Found : C, 78.01 ; H, 10.9. $C_{20}H_{34}O_2$ requires C, 78.4 ; H, 11.1%).

2-n-*Octyl*-4 : 5-*dimethoxybenzaldehyde*.—Dry HCl gas was passed through a mechanically stirred mixture of 3 : 4-dimethoxy-*n*-octylbenzene (16 g.), zinc cyanide (12 g.) and dry benzene (110 c.c.) at 0° for 1 hour. Powdered $AlCl_3$ (anhyd., 8 g.) was then added and the passage of HCl gas was continued. After 3 hours, the temperature was raised to 40-45°, maintained for ½ hour and finally kept at 50-60° for 2 hours. The mass was then left overnight, decomposed by ice, and refluxed for half an hour. Benzene layer was separated and the aqueous solution was further extracted with benzene. From the combined benzene solution the aldehyde was obtained by distillation ; b.p. 170-72°/0.4 mm, yield 6 g. (33.7%).

The 2 : 4-*dinitrophenylhydrazone* was crystallised from alcohol in fine red needles, m.p. 185-86°. (Found : N, 12.5. $C_{23}H_{30}O_6N_4$ requires N, 12.23%).

2-n-*Decyl*-4 : 5-*dimethoxybenzaldehyde*.—B.p. 192-94°/0.4 mm, yield 20%. The aldehyde solidified on cooling. The 2 : 4 *dinitrophenylhydrazone* was crystallised from alcohol in red needles, m.p. 167-69°. (Found : N, 11 8. $C_{25}H_{34}O_6N_4$ requires N, 11.53%).

2-n-*Dodecyl*-4 : 5-*dimethoxybenzaldehyde*.—B.p. 210-12°/1 mm, yield 32% ; 2 : 4-*dinitrophenylhydrazone* was crystallised from alcohol in red needles, m.p. 151-52°. (Found : N, 11.1. $C_{27}H_{38}O_6N_4$ requires N, 10.89%).

2-n-*Hexyl*-4 : 5-*dimethoxy*-β-*nitrostyrene*. —2-*n*-Hexyl-4 : 5-dimethoxybenzaldehyde (7 g.) and nitromethane (1.5 c.c.) were dissolved in alcohol (15 c.c.) and cooled to 5°. To this solution was then slowly added with vigorous stirring an alcoholic KOH solution (3 g. in 25 c.c. alcohol), previously cooled to 5°. The addition was completed in ten minutes and the temperature was not allowed to rise above 15°. After an hour ice-water was added to dissolve the precipitated solid and this solution was then poured with stirring in dilute HCl (10 c.c., conc. HCl in 100 c.c. water). The mass was left for a few hours and filtered. It was crystallised from alcohol in yellow

prismatic needles, m.p. 73-74°, yield 4 g. (Found : C, 65.2 ; H, 8.1. $C_{16}H_{23}O_4N$ requires C, 65.5 ; H, 7.84%).

2 n-*Octyl*-4 : 5-*dimethoxy*-β-*nitrostyrene* was crystallised from alcohol in yellow needles, m.p. 74-75°, yield 20%. (Found : C, 67.5 ; H, 8.3. $C_{18}H_{27}O_4N$ requires C, 67.3 ; H, 8.4%).

2 n-*Decyl*-4 : 5-*dimethoxy*-β-*nitrostyrene* was crystallised from alcohol in yellow needles, m.p. 78-80°, yield 51%. (Found : C, 68.4 ; H, 8.9. $C_{20}H_{31}O_4N$ requires C, 68.77 ; H, 8.88%).

2-n-*Dodecyl*-4 : 5-*dimethoxy*-β-*nitrostyrene* was crystallised from alcohol in yellow needles, m.p. 76-78°, yield 36%. (Found : C, 69.8 ; H, 9.1. $C_{22}H_{35}O_4N$ requires C, 70.03 ; H, 9.28%).

β-(2-n-*Hexyl*-4 : 5-*dimethoxyphenyl*)-*ethylamine Hydrochloride*.—2-*n*-Hexyl-4 : 5-dimethoxy-β-nitrostyrene (0.01*M*), dissolved in anhydrous ether, was gradually poured into a suspension of $LiAlH_4$ (0.04*M* of commercial variety) in ether. After the addition was over, the mixture was refluxed for 4 hours, cooled and the excess of $LiAlH_4$ was decomposed with water. The ethereal solution of the amine was filtered, the residual solid was extracted with ether and the combined ethereal solution was washed with water, dried (Na_2SO_4) and saturated with dry HCl gas. The precipitated hydrochloride was filtered and crystallised from a mixture of absolute alcohol and ethyl acetate in colorless needles, m.p. 124°, yield 40% of theoretical. Mixed m.p. with our previous sample (*loc. cit.*, p. 617) was undepressed.

β-(2-n-*Octyl*-4 : 5-*dimethoxyphenyl*)-*ethylamine hydrochloride* was crystallised from ethyl acetate in colorless needles, m.p. 120°, yield 33%. (Found : N, 4.4. $C_{18}H_{32}O_2NCl$ requires N, 4.25%). The *picrate* was crystallised from alcohol in fine needles, m.p. 125-26°.

β-(2-n-*Decyl*-4 : 5-*dimethoxyphenyl*)-*ethylamine hydrochloride* was crystallised from ethyl acetate in colorless needles, m.p. 111°, yield 25% of theoretical. (Found : N, 4.02. $C_{20}H_{36}O_2NCl$ requires N, 3.9%). The *picrate* was crystallised from alcohol in brown needles, m.p. 123-24°.

β-(2-n-*Dodecyl*-4 : 5-*dimethoxyphenyl*)-*ethylamine hydrochloride* was crystallised from ethyl acetate in colorless needles, m.p. 117-19°, yield 25% of theoretical. (Found : N, 3.7. $C_{22}H_{40}O_2NCl$ requires N, 3.63%). The *picrate* was crystallised from alcohol in brown needles, m.p. 126°.

2-n-*Octyl*-4 : 5-*dimethoxy acetophenone*.—A mixture of acetyl chloride (3 g.), $AlCl_3$ (anhyd., 12 g.) and CS_2 (25 c.c.) was cooled in an ice-bath for half an hour. To this mixture was slowly added with shaking 1-*n*-octyl-3 : 4-dimethoxybenzene (9 g.). The mass was left overnight and later on heated on a water-bath till HCl had ceased to evolve. CS_2 was removed by distillation and the mass was decomposed with ice. It was then extracted with benzene, the demethylated product was extracted out with NaOH solution which was subsequently methylated, and the combined product was distilled ; b.p. 158-62°/0.4 mm, yield 30% of theoretical. (Found : C, 73.6 ; H, 9.3. $C_{18}H_{28}O_3$ requires C, 73.98 ; H, 9.59%). The semicarbazone could not be prepared in solid state.

2-n-*Decyl*-4 : 5-*dimethoxy-acetophenone* boiled at 168-70°/0.4 mm, yield 35% of theoretical. (Found : C, 74.8 ; H, 10.3. $C_{20}H_{32}O_3$ requires C, 75.01 ; H, 10.0%).

2-n-*Dodecyl*-4 : 5-*dimethoxy-acetophenone* was distilled at 198-200°/0.4 mm, yield 25% of theoretical. (Found : C, 75.50; H, 10.20. $C_{22}H_{36}O_3$ requires C, 75.86 ; H, 10.35%).

α-(2-n-*Octyl*-4:5-*dimethoxyphenyl*)-*ethylamine Hydrochloride*.—Crude 2-*n*-octyl-4:5-dimethoxy-acetophenone oxime was reduced with sodium in absolute alcohol. The reduced mass was made acidic with HCl (conc.), alcohol was removed by distillation under reduced pressure and the precipitated sodium chloride was dissolved in minimum amount of water. It was filtered and the residual crude hydrochloride was washed with benzene and crystallised from hot water in colorless short needles, m p. 162-63°. (Found : N, 4.3. $C_{18}H_{32}O_2NCl$ requires N, 4.25%). The *picrate* was crystallised from alcohol in brown needles, m.p. 180°.

α-(2-n-*Decyl*-4 : 5-*dimethoxyphenyl*)-*ethylamine Hydrochloride*.—Crude 2-*n*-decyl-4 : 5-dimethoxyphenyl-acetophenone oxime was reduced in the usual manner. The hydrochloride was crystallised from hot water in short needles, m.p. 150-52°. (Found : N, 4.1. $C_{20}H_{36}O_2NCl$ requires N, 3.9%). The *picrate* was crystallised from dilute alcohol in brown needles, m.p. 146-48°.

α-(2-n-*Dodecyl*-4 : 5-*dimethoxyphenyl*)-*ethylamine hydrochloride* was crystallised from hot water in colorless needles, m.p. 144°. (Found : N, 3.8. $C_{22}H_{40}O_2NCl$ requires N, 3.63%). The *picrate* was crystallised from dilute alcohol in brown needles, m.p. 160-61°.

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Department of Applied Chemistry,
The Calcutta University,
Calcutta-9.

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CHEMISTRY OF BERYLLIUM. PART VI. COMPOUNDS OF BERYLLIUM CHLORIDE WITH UREA, BENZAMIDE, THIOUREA AND SUBSTITUTED THIOUREAS

By Sarju Prasad and Kashi Prasad Srivastava

The formation of the complex compounds of beryllium chloride with urea, benzamide, thiourea, phenyl-, *o*-, *m*- and *p*-tolyl-,diphenyl- and *o*-, *m*- and *p*-ditolyl-thioureas in organic solvents has been studied and their structures have been discussed.

A survey of literature shows that no work has been done on the formation of complex compounds of beryllium chloride with urea, amides and thioureas. The present work was therefore undertaken with a view to studying the formation of complex compounds of beryllium chloride with urea, benzamide, thiourea and symmetrical as well as unsymmetrical thioureas.

Experimental

Anhydrous beryllium chloride was prepared, as reported in an earlier paper (this *Journal*, 1957, **34**, 317).

An alcoholic solution of urea or benzamide was taken in a well-corked conical flask and an ethereal solution of $BeCl_2$ added slowly with constant stirring. The mixture was shaken well for sometime, excess of the solvent distilled off and the mother-liquor allowed to crystallise in vacuum. With urea, the complex compound separated out first, which was recrystallised from absolute alcohol, but in the case of benzamide, it crystallised out first and then the complex compound separated out at a low temperature in white square plates from the mother-liquor.

Similar procedure was followed in the preparation of thiourea and substituted thiourea complexes. In each of the cases, when the mixture was cooled the unchanged thiourea crystallised out first. The complex compound separated out from the mother-liquor after keeping it for several days in a vacuum desiccator.

Complex compounds of beryllium chloride with urea and benzamide were also prepared in ether medium by adding a known weight of urea or benzamide to the excess of $BeCl_2$ in ether and then shaking the mixture for several hours. After the reaction was over, the supernatant liquid was decanted off and the compounds obtained were washed several times with dry ether. These were first dried between the folds of filter paper and finally in vacuum.

When the same procedure was followed, thiourea and substituted thioureas formed no compounds.

Beryllium, chloride and nitrogen were estimated by using the same methods as described in Part II (*loc. cit.*). Sulphur was estimated by the fusion method.

General Properties.—Urea and benzamide complexes are white in colour, not hygroscopic and melt at 213-14° and 107-109° respectively. The complex compounds

obtained with thiourea and substituted thioureas are all coloured, very hygroscopic and decompose readily in air. These are insoluble in common organic solvents but are soluble in alcohol.

TABLE I

Amides and thioureas.	% Be. Found.	% Be. Calc.	% Cl. Found	% Cl. Calc.	% Nitrogen. Found.	% Nitrogen. Calc.	Colour.	Compound.
1. Urea	2.91	2.81	22.20	22.19	34.81	35.00	White	$BeCl_2.4NH_2.CO.NH_2$
2. Benzamide	2.80	2.79	22.01	22.05	8.62 % Sulphur.	8.66	Do	$BeCl_2.2C_6H_5.CO.NH_2$
3. Thiourea	3.80	3.88	30.17	30.60	27.64	27.58	Yellow	$BeCl_2.2NH_2.CS.NH_2$
4. Phenyl-T*	3.83	3.88	30.17	30.60	13.72	13.7	Light yellow	$BeCl_2.C_6H_5NH.CS.NH_2$
5. *o*-Tolyl-T	3.61	3.66	28.80	28.86	12.94	13.01	Light pink	$BeCl_2$ *o* Tol.-NH.CS.NH_2
6. *m*-Tolyl-T	3.60	3.66	28.80	28.86	12.94	13.01	Do	$BeCl_2.m$-Tol.-NH.CS.NH_2
7. *p*-Tolyl-T	3.64	3.66	28.82	28.86	12.97	13.01	Do	$BeCl_2.p$-Tol.-NH.CS.NH_2
8. Diphenyl-T	2.90	2.92	23.02	23.05	10.34	10.39	Light yellow	$BeCl_2$.PhNH.CS.NH.Ph
9. *o*-Ditolyl-T	2.62	2.68	21.04	21.13	9.47	9 52	Pink	$BeCl_2.o$-$CH_3C_6H_4NH.CS.NH.C_6H_4.CH_3$
10. *m*-Ditolyl-T	2.64	2.68	21.04	21.13	9.50	9.52	Do	$BeCl_2.m$-$CH_3C_6H_4NH.CS.NH.C_6H_4.CH_3$
11. *p*-Ditolyl-T	2.64	2.68	21.06	21.13	9.48	9.52	Do	$BeCl_2.p$-$CH_3C_6H_4NH.CS.NH.C_6H_4.CH_3$

*T denotes thiourea

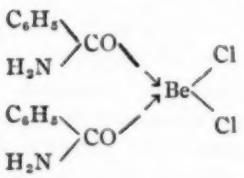
DISCUSSION

Beryllium chloride forms a crystalline stable complex in which four molecules of urea combine with one molecule of beryllium chloride. The carbonyl group present in the urea molecule being very reactive and also the affinity of beryllium towards oxygen being strong, it appears that chlorine is readily displaced to the outer ring, as has been observed by Ephraim and Biltz (*Ber.*, 1912, **45**, 1323, 1330; *Z. physikal. Chem.*, 1913, **81**, 532; Z. *anorg. Chem.*, 1925, **148**, 157; 1927, **166**, 341) in the case of ammonia and by Fricke and Havestadt (*Z. anorg. Chem.*, 1925, **146** 121; 1926, **152**, 357) in the case of methylamine and ethylenediamine. The compound may be represented as:

$$\left[\begin{matrix}(NH_2)_2CO \searrow \\ (NH_2)_2CO \nearrow\end{matrix} Be \begin{matrix}\swarrow OC(NH_2)_2 \\ \nwarrow OC(NH_2)_2\end{matrix}\right] Cl_2$$

It is interesting to note that only two molecules of benzamide combine with one molecule of $BeCl_2$. It appears that the aromatic group present in the benzamide molecule offers steric hindrance and the carbonyl group becomes sufficiently weak to displace chlorine to the outer ring. The octet of the beryllium is completed by two

co-ordinate links from -CO- group in which oxygen acts as the donor and the two covalent links of the chlorine. The compound can be represented as:

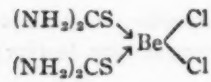


The result is similar to our previous work on compounds of amines with beryllium chloride (*loc. cit.*) and also of other workers (Fricke *et al.*, *Z. anorg. Chem.*, 1925, **146**, 103, 121; 1926, **152**, 347, 357; 1927, **163**, 31; 1928, **170**, 125) who observe that the aromatic amines form only diamines and only two molecules of benzaldehyde combine with one molecule of $BeCl_2$ (Fricke and Havestadt, *loc. cit.*).

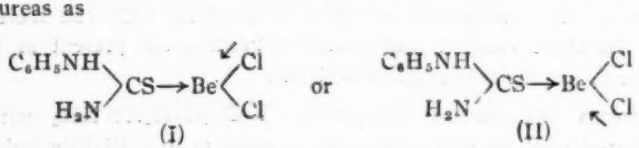
Thiocarbamide readily forms complex compounds with different metallic salts (Maly, *Ber.*, 1876, **9**, 172; Rosenheim and Meyer, *Z. anorg. Chem.*, 1906, **49**, 13; Mussgnug and Vanino, *Ber.*, 1917, **50**, 21; Haworth and Mann, *J. Chem. Soc.*, 1943 661) in which one, two or three molecules of thiourea combine with one molecule of the metallic salt. In these complex compounds sulphur atom present as thiocarbonyl group acts as the donor, forming stable complexes.

Thiourea forms the complex compound $BeCl_2.2NH_2.CS\,NH_2$ with beryllium chloride in ether-alcohol mixture, but not in water or in a slightly acidic solution. It is similar to the complex compounds of $ZnCl_2$, $CdCl_2$ and $HgCl_2$ (Maly, *loc. cit.*; Rosenheim and Meyer, *loc. cit.*) in many respects, but differs from them in being hygroscopic and readily hydrolysable.

Though both nitrogen and sulphur are present in the molecule yet co-ordination through sulphur has been suggested in all these cases (vide references cited above). Morgan and Burstall (*J. Chem. Soc.*, 1928, 145) suggest that the thiourea complexes, in which sulphur of the thiocarbonyl and nitrogen of the amino group co-ordinate, are highly complex in nature and usually the compounds contain more than one metal atoms combined with several molecules of the thiocarbamide. Sahasrabudhey and Krall (this *Journal*, 1942, **19**, 25; 1944, **21**, 63) observed that the formation of complex compounds between cupric sulphate and phenylthiocarbamide was largely influenced by temperature and suggested that the co-ordination occurred exclusively through sulphur atom. Even in its reaction with nitrous acid (Sahasrabudhey and Krall, *loc. cit.*), $-NH_2$ group present in phenylthiocarbamide is not attacked but oxidation occurs and the nitro derivative of Hector's base is formed. It seems probable that the $-NH_2$ groups in thiourea are not 'amino' in the conventional sense, as is evident from the fact that salts of the type of amine hydrochloride are not known. Further, the complex compound, $BeCl_2.2(NH_2)_2CS$, is very hygroscopic, which goes to prove beyond doubt that the co-ordination is not through nitrogen as the amino complexes are sufficiently stable. From these considerations it appears that the co ordination is through sulphur, and the compound may be represented as:

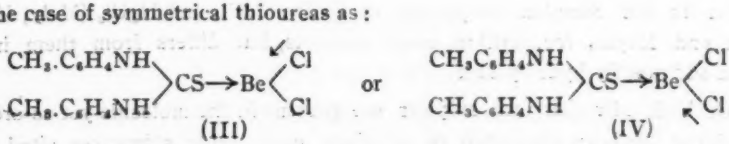


It is surprising that only one molecule each of unsymmetrical and symmetrical thioureas combines with one molecule of beryllium chloride. Beryllium chloride molecule is supposed to be sp^2 hybridised (Cartmell and Fowles, "Valency and Molecular Structure", p. 147). On the approach of a pair of electrons, the mode of hybridisation changes to the sp^3 state. Out of the two vacant orbitals, one is filled up by a lone pair of electrons from the sulphur atom (perhaps the second molecule of the thioureas does not take part in co-ordination due to steric reasons). As the beryllium atom readily assumes the maximum covalency of four, it seems probable that one of the chlorine atoms donates a lone pair of electrons (for filling up the second vacant orbital) as back co-ordination rather than the second pair being derived from the same sulphur atom. Similarly, Goremykin and Gladyshevskaya (*J. Gen. Chem. USSR.*, 1942, **13**, 762; 1944, **14**, 13) suggested polynuclear structures involving hydrazine bridges in preference to chelate structures in the case of $PtCl_2(N_2H_4)$ and $PdBr_2(N_2H_4)$. Thus, the compounds may be represented in the case of unsymmetrical thioureas as



(I) (II)

and in the case of symmetrical thioureas as :



(III) (IV)

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CHEMICAL LABORATORIES,
BANARAS HINDU UNIVERSITY,
VARANASI-5.

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DECOMPOSITION OF ORGANIC HALOGEN COMPOUNDS BY ULTRASONIC WAVES. PART II. MECHANISM OF THE DECOMPOSITION OF METHYLENE DICHLORIDE IN AQUEOUS SOLUTIONS

By Satya Prakash and Satish Chandra Srivastava*

Aqueous solutions of CH_2Cl_2, subjected to ultrasonic waves (1·2 Mc/s, 225 watts electrical input to the transducer) liberate chlorine (0·0149 g. atom per g. mole of CH_2Cl_2 in 3 hours) with the simultaneous formation of a yellow-coloured solid. With longer exposures, the liberation of chlorine does not seem to increase much. Pure undiluted CH_2Cl_2 fails to be decomposed by the waves. However, with dilution the liberation of chlorine increases and finally reaches a value of 1·403 g. atom per g. mole of CH_2Cl_2 at 0·1% approx. A considerable amount of bulk effect is observed. The decomposition is of zero order to a greater extent at both the frequencies tried and is favoured at the lower frequency. The reactions proposed are :

$$H.OH \rightarrow H^+ + OH^-$$
$$CH_2Cl_2 \rightarrow CH_2Cl^+ + Cl^-$$

followed by hydrolysis and polymerisation.

Schmidt, Johnson and Olson (*J. Amer. Chem. Soc.*, 1929, **51**, 370), while studying the oxidising action of ultrasonic waves, observed that aqueous carbon tetrachloride containing potassium iodide and starch became intensely blue ; carbon tetrachloride and silver potassium bromide (two phase system) imparted a yellow coloration to water.

A similar observation was recorded by Liu and Wu (*ibid.*, 1934, **56**, 1005) who remarked that the activated oxygen, produced under the influence of ultrasonic waves, liberated chlorine from carbon tetrachloride and chloroform in aqueous solutions. Kling and Kling (*Compt. rend.*, 1946, **223**, 1131), while studying the influence of ultrasonic waves on halogen-substituted hydrocarbons, reported the liberation of halogens in detectable quantities which could be tested with silver nitrate solutions. The rupture of C—Cl bond was also observed by Surova (*Doklady, SSSR.*, 1953, **90**, 1083) while studying the decomposition of the aqueous solutions of sucrose in presence of carbon tetrachloride under the influence of ultrasonic waves and they further stated that no cleavage of C—Cl bond took place in non-aqueous medium. The decomposition of aqueous solutions of carbon tetrachloride by ultrasonic waves was studied by Weisler *et al.* (*J. Amer. Chem. Soc.*, 1950, **72**, 1769) and they proposed a mechanism also.

In a series of papers the present authors have attempted a study of the decomposition of organic halides under the influence of ultrasonic waves, e.g., carbon tetrachloride, methylene dichloride ethylene dichloride and dibromide and chloroform. It has been observed that none of them except chloroform decomposes in pure state whereas all of them liberate halogens, when subjected to ultrasonic waves in aqueous solutions, in ionic as well as molecular form and simultaneously produce polymerised solids.

In the present paper, the sono-chemical decomposition of methylene dichloride has been studied which is comparatively a simple substance. It is a liquid, having b.p. 40° and a solubility of 2 g./100 c.c. in water.

Methylene dichloride also furnishes solid products in traces when subjected to ultrasonic waves. This product is very much similar to the one obtained in the case of

*Present address : Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-32.

ethylene dichloride. This may be due to the breaking of a C—Cl bond and thereafter to the presence of (CH_2Cl) radical in the former case and to CH_2CH_2Cl in the latter ; these free radicals finally polymerise to solid products.

It is of interest to point out here that methylene dichloride in pure undiluted form did not dceompose under the influence of ultrasonic waves. The pure sample was taken in an H-shaped tube ; one arm containing the sample and the other, indicator for chlorine or chloride ions, and the waves were passed for half an hour. No traces of free halogen or halide ion could be detected qualitatively.

The experimental results on the decomposition of methylene dichloride by ultrasonic waves are recorded under the following heads :

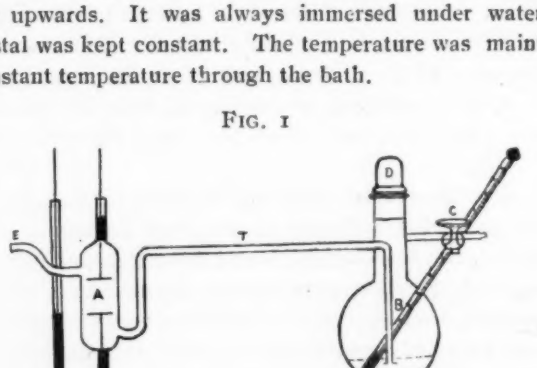
(1) The effect of concentration and bulk on the decomposition.
(2) The kinetics of the decomposition at two frequencies.

Experimental

The source of ultrasonic power, as in the previous communication (Prakash and Srivastava, *Z. physikal. Chem.*, 1957, **208**, 127), was a high frequency ultrasonic generator (Mullard Type E-7562) with a 1.5 K watt oscillator, generating up to a maximum of 375 watts radio frequency when used with a 2-inch circular disc of barium titanate transducer. All the work was done at 225 watts electrical input to the transducer and frequencies of 990 Kc/s and 2100 Kc/s. These frequencies were the resonant frequencies of the transducers and were measured with a sufficiently accurate wave-meter. At these frequencies there were maximum fountain and fog of liquid vapours inside the reaction vessel. The output of the oscillator was fixed by using a stabilised line supply.

The transducer was introduced in a bath horizontally so that the waves could be produced vertically upwards. It was always immersed under water and the level of water above the crystal was kept constant. The temperature was maintained by circulating water at a constant temperature through the bath.

Fig. 1

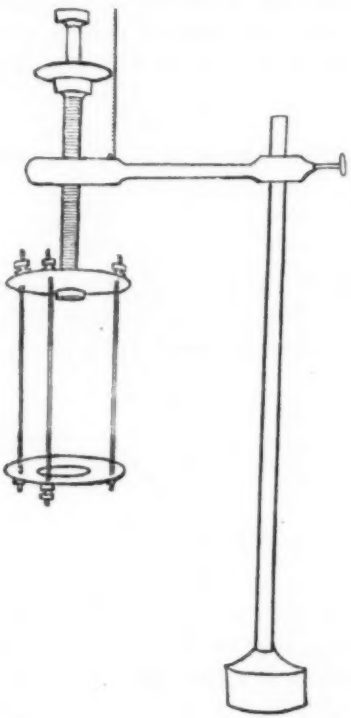


The most suitable reaction vessel was found to be a flat-bottomed ground glass stoppered pyrex flask of 100 c.c. capacity for 2100 Kc/s transducer and (flat bottomed ground glass stoppered) Jena bottle of 250 c.c. capacity for 990 Kc/s transducer. In conductivity experiments, a specially desigued reaction vessel, as shown in Fig. 1, was

used. This enabled observations to be made at any desired time without stopping the generator, by sucking up the solution in the conductivity cell for a short interval and then again sending it back to the reaction vessel.

The reaction flask was clamped between two brass plates, the lower one was provided with a circular hole of diameter of 2 inches. The distances between the plates could be varied at will, according to the size of the reaction vessel, with the help of a nut and thread device. The upper plate was fixed to a long range spherometer which could move up to 6 inches with a least count of 0.0001 inches. The spherometer was attached to a stand and could be moved up and down. The arrangement of clamp and stand is shown in Fig. 2.

FIG. 2



The results were reproducible up to 6%, as shown in a previous communication Srivastava, *Vijnaan Parishad Anusandhan Patrika* 1958, **1**, 191).

Estimation of Liberated Chlorine as Silver Chloride in the Decomposition of Methylene Dichloride.—Saturated solutions of G. R. Merck quality methylene dichloride were prepared in water and portions of 20 c.c. of these solutions were exposed to ultrasonic waves at 35° for different periods. The reaction mixtures after exposure were kept for sometime to allow the finely divided particles to settle down and then these were filtered. The filtrates were estimated gravimetrically for chloride after the conversion

of free chlorine and hypochlorous acid formed, if any, into hydrochloric acid by reduction with sulphurous acid. The results are recorded in Table I.

TABLE I

Frequency = 2100 Kc/s. Power input = 225 watts. Temp. = 35°.
Vol. of soln. = 20 c.c. CH_2Cl_2 taken = 0.40 g.

Exposed for (in hr.)	½	1	1½	2	2½	3	3½
AgCl formed (g).	0.0028	0.0030	0.0036	0.0056	0.0080	0.0100	0.0102
Cl in CH_2Cl_2 (g. atom/g. mole)	0.0042	0.0045	0.0054	0.0085	0.0121	0.0149	0.0160

Effect of Concentration on the Decomposition of Methylene Dichloride.—Methylene dichloride solutions in 4 different concentrations were prepared by adding water to saturated solutions, and 20 c.c. portions of each of these solutions were exposed to ultrasonic waves for a period of 3 hours. The liberated chlorine was estimated gravimetrically as silver chloride, as described in the previous section. The results are recorded in Table II.

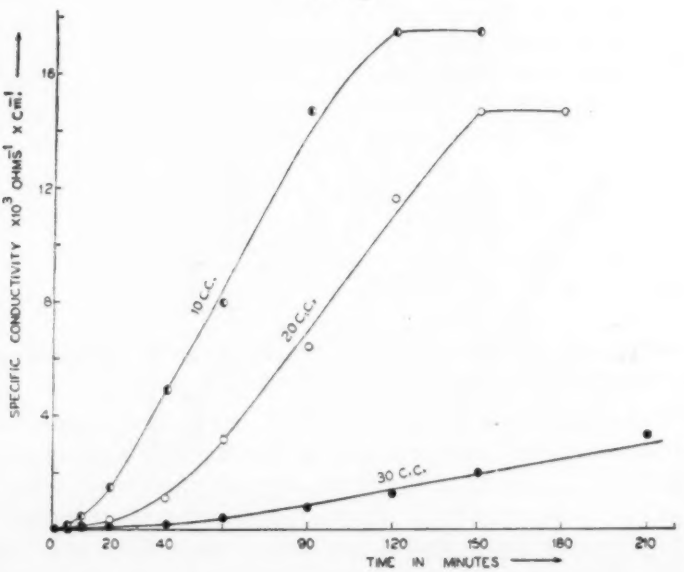
TABLE II

[Conditions same as in Table I excepting CH_2Cl_2].

CH_2Cl_2 taken (g.)	0.4000	0.2000	0.1000	0.0200
AgCl formed (g.)	0.0100	0.0266	0.0486	0.0474
Cl in CH_2Cl_2 (g. atom/g. mole)	0.0149	0.0790	0.2887	1.4030

Effect of Bulk on the Decomposition of Methylene Dichloride.—Different volumes of saturated solutions of methylene dichloride were exposed to ultrasonic waves and changes in conductivity with time were noted. The results are shown in Fig. 3.

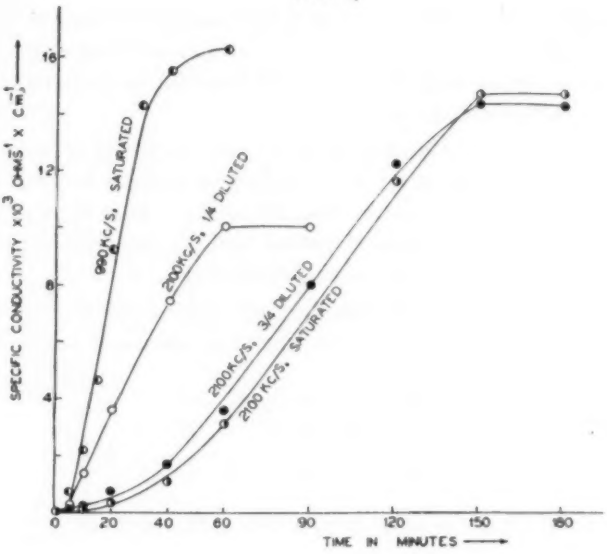
FIG. 3



Determination of the Kinetics of the Reaction.—A saturated solution of G.R. Merck quality of methylene dichloride was prepared in conductivity water (conductivity 2.2×10^{-6}). Then 15 c.c. and 5 c.c. portions of the saturated solutions were made up to 20 c.c. by adding conductivity water ; 20 c.c. portions of the saturated solution and each of the subsequently prepared solutions were exposed to ultrasonic waves and the changes in conductivity were noted. The results are shown in Fig. 4.

The same experiment was repeated with a saturated solution of methylene dichloride at 990 Kc/s, as shown in Fig. 4.

FIG. 4



DISCUSSION

From the observations recorded in Table I, it is clear that with the saturated solution of methylene dichloride (about 2%) the amount of chlorine liberated per g. mole of the substance during the course of 3 hours of ultrasonic exposure (225 watts input and 2100 Kc/s) is about 0.0 5 g. atom, and with the increased exposure, it does not appear to be increased much.

The results recorded in Table II, however, show that if dilute solutions of methylene dichloride are taken, the amount of chlorine liberated is finally raised to 1.4 g. atom/g. mole of the substance at about 0.1% approximately. If the total halogen is released, as may be expected at higher dilutions, the value should be finally 2 g. atom of chlorine per g. mole of methylene dichloride.

Mechanism of the Decomposition.—It may be expected that the reaction proceeds in three different ways simultaneously. One of the fundamental sono-chemical reactions is believed to be the decomposition of water, as shown by the reaction (Prudhome

et al., *J. chim. phys.*, 1953, **50**, 107 ; 1950, **47**, 795 ; 1949, **46**, 323 ; Weisler *et al.*, Chem. Eng. Progress Symposium, No. 1, p. 47 ; Hughes, *J. Chem. Soc.*, 1936, 225; 1935, 255 ; 1937, 1183 ; Frensdorff and Clark, *J. chim. phys.*, 1950, **47**, 399 ; Hine, *J. Amer. Chem. Soc.*, 1950, **72**, 2438) :

$$H.OH \rightarrow H^+ + OH^- \quad \ldots \quad \ldots \quad (1)$$

involving the breaking of H and OH with the consumption of 118 K cals. per g. mole. Simultaneously the sono-chemical decomposition of methylene dichloride may take place as shown below :

$$CH_2Cl_2 \rightarrow CH_2Cl^+ + Cl^- \quad \ldots \quad \ldots \quad (2)$$

This necessitates the consumption of 68 K cals. for the breaking of C—Cl bond.

Following these two reactions, a number of side reactions may take place. Two types of mechanism may be suggested : one involving the hydrolysis and oxidation and the other, polymerisation and chain termination.

Hydrolysis and Oxidation Mechanism.—In order to explain the various steps it will be interesting to follow, at least so far as the hydrolysis is concerned, the chains postulated by Hughes and co-workers (*loc. cit.*) (SN_1, SN_2 & E_2). Here it may be of interest to refer the three alternative mechanisms described by Hine (*loc. cit.*) for the basic hydrolysis of chloroform, suggesting CCl_2^+ as an intermediate.

Assuming the reaction (1) to be the primary sono-chemical reaction followed by the hydrolysis of methylene dichloride, promoted by ultrasonic waves, the following set of reactions may be suggested :

$$CH_2Cl_2 + OH^- \rightarrow CH_2ClOH + Cl^- \quad SN_2 \quad \ldots \quad (3)$$

$$\left.\begin{array}{ll} CH_2Cl_2 \rightarrow CH_2Cl^+ + Cl^- & \\ CH_2Cl^+ + OH^- \rightarrow CH_2ClOH & \end{array}\right\} \; SN_1 \quad \ldots \quad (4) \text{ and } (5)$$

followed by :

$$CH_2Cl(OH) + OH^- \rightarrow HCHO + H.OH + Cl \quad (6)$$

The radicals Cl and H, formed in the sono-chemical reactions, may combine to give :

$$Cl^- + Cl^- \rightarrow Cl_2 \quad (7)$$

$$H^+ + Cl^- \rightarrow HCl \quad (8)$$

Polymerisation and Chain Termination.—Assuming the primary sono-chemical reaction to be one expressed by the reaction (2), the following reactions may be suggested to be taking place :

$$CH_2Cl_2 \rightarrow CH_2Cl^+ + Cl^- \quad \ldots \quad \ldots \quad (9)$$

$$2CH_2Cl \rightarrow \begin{matrix} CH_2Cl \\ | \\ CH_2Cl \end{matrix} \rightarrow CH_2 = \overset{\overset{X}{|}}{\underset{\underset{Y}{|}}{C}} \rightarrow CH_2-\overset{\overset{X}{|}}{\underset{\underset{Y}{|}}{C}}-(CH_2-\overset{\overset{X}{|}}{\underset{\underset{Y}{|}}{C}}-)_n \quad \ldots \quad (10)$$

where X and Y may be Cl or H.

$$CH_2Cl_2 + Cl^- \rightarrow CHCl_2^- + HCl \quad \ldots \quad \ldots \quad (11)$$

$$CHCl_2^- + H^+ \rightarrow CH_2Cl_2 \quad \ldots \quad \ldots \quad (12)$$

Kinetics of the Reaction.—The kinetics of the reaction at 2100 Kc/s is of zero order, which indicates that the reaction is proportional to the intensity of waves. This is analogous to perfect photochemical reactions in which the velocity is proportional to the intensity of light. The graph indicating the changes in electrical conductivity with time for three concentrations of methylene dichloride have been plotted in Fig. 4 and these are straight lines. It is clear from Fig. 4 that the reaction is favoured at a lower frequency.

CHEMICAL LABORATORIES,
THE UNIVERSITY OF ALLAHABAD,
ALLAHABAD.

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ERRATA

Page	Line	*Read*	*For*
60	Table IV, Column, 1 lines 2 & 3	in %).	in g.).
251	8	1908, **93**, 745	1908, **93**, 735
252	5	1957, **34**, 35	1947, **34**, 35
253	32	m.p. 213–15°	m.p. 213–25°
501	Table III, last line, Column 5	28.0	0.28
	„ 6	25.0	0.25
675	21	5.6×10^9	5.6
709	23	the last two	the last three

MODIFICATION OF DROP WEIGHT METHOD FOR MEASURING SURFACE AND INTERFACIAL TENSION OF LIQUIDS

By P. M. Krishna and D. Venkateswarlu

The procedure and apparatus adopted by Harkins *et al.* have been used for the rapid and accurate determination of surface and interfacial tension of a number of liquids. The values obtained agree closely with those available in the literature.

In the drop weight method of Harkins *et al.* (*J. Amer. Chem. Soc.*, 1919, **41**, 499; 1916, **38**, 228, 236, 242), the application of suction to the receiving vessel is inconvenient and the variation in liquid head lowers the drop size in the course of a determination. The apparatus and procedure described herein overcome these limitations.

Experimental

A capillary pipette, the details and dimensions of which are shown in Fig. 1(a), is constructed of a 2 mm I.D. straight pyrex tubing. The nozzle N is polished with a fine emery paper to get a sharp tip of circular cross section. The stop-cock S is located such that the test liquid does not come into contact with the stop-cock grease. The wooden board (on which a cm. graph paper is pasted) supports the pipette and enables it to be hooked from laboratory stands.

Fig. 1

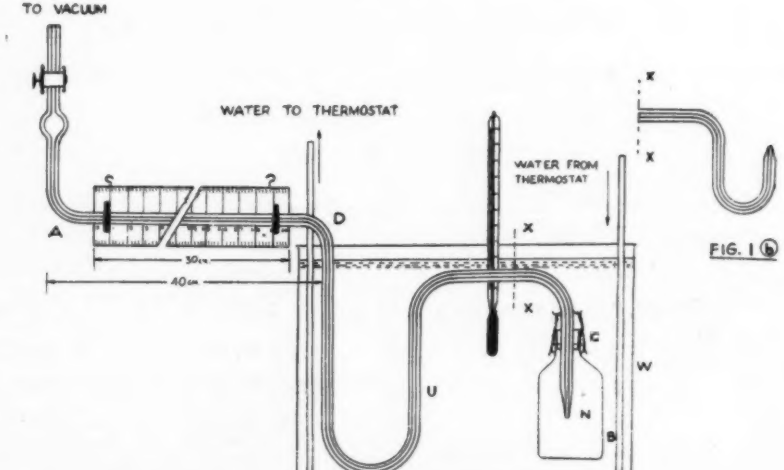

FIG. 1 (a)

To determine the surface tension of a liquid, it is sucked into the clean dry pipette and the bottle 'B' is securely held in position. After allowing sufficient time for the liquid in the U bend to attain the temperature of the water-bath 'W', three or four drops are released from the tip very slowly by careful manipulation of the vacuum. Thus, the drops attain the temperature of the water-bath before reaching the nozzle tip. All the drops are released under the same liquid head. The volume of the drops released is taken from the change in meniscus in the calibrated horizontal section 'AD' as fluid displacement is independent of temperature.

In determining the interfacial tension between two liquids, the heavier liquid is taken into the pipette and the lighter liquid into the bottle. Alternatively, a pipette with the tip pointing upwards, as shown in Fig. 1(b), is used and is found to furnish good results.

From the average drop volume, the surface tension is determined by the equation

$$\sigma = \frac{V \rho g}{2 \pi r \psi} \qquad \ldots \qquad \ldots \quad (1)$$

(where σ = surface tension in dynes/cm, V = volume of drop in c.c., ρ = density of liquids in g./c.c., g = acceleration due to gravity, 981 cm/sec^2., π = a const., 3.1416, r = radius to tips in cm and ψ = function of $r/V^{1/3}$) using the same corrections factor ψ, as Harkins *et al.* (*loc. cit.*, 1919) since drops are formed under the same condition. For interfacial tension, $\Delta\rho$ is used in place of ρ in equation (1).

The surface and interfacial tension values of some organic liquids, determined at 20° using the apparatus and procedure described herein, are recorded in Tables I and II, along with the standard values reported in the International Critical Tables (Vol. IV, pp. 432-475). Table III shows the interfacial tension values of some liquids in contact with water at different temperatures. These tables and the surface tension values of some liquids, determined at different temperatures, show that the deviations are within the limits of experimental error.

TABLE I

Surface tension of liquids at 20°.

Liquid.	Density.	Surface tension.		
		Found.	Lit.	% Diff.
1. Acetylene tetrabromide	2.9630	49.76	49.67 ± 0.1	0.18
2. Benzene	0.8792	28.92	28.88 ± 0.05	0.14
3. CCl_4	1.5910	26.67	26.77 ± 0.1	0.37
4. Chlorobenzene	1.1040	33 09	33.19 ± 0.1	0.30
5. Ethylene dibromide	2.1800	38.90	38.75 ± 0.1	0.39
6. *n*-Hexane	0 6814	18.65	18.43 ± 0.2	0.11*
7. Methyl-*n*-propyl ketone	0.8110	25.05	25.20 ± 0.5	0.60
8. Nitrobenzene	1.2040	43.98	43.90 ± 0.5	0.18
9. *o*-Nitrotoluene	1.1640	41.38	41.46 ± 0.2	0.04
10. *m*-Nitrotoluene	1.1570	40.76	40.90 ± 0.2	0.34
11. Toluene	0.8638	28.45	28.43 ± 0.05	0.07
12. Water	0.9983	72.90	72.75 ± 0.05	0.21

* The deviation is 0.11 % if literature value is taken as 18.63. If the mean value is taken as the basis, the deviation is 1.19%.

TABLE II

Interfacial tension of liquids in contact with water at 20°.
(Density of distilled water at 20° = 0.9982 g./c.c.).

	Liquid.	Density.	Interfacial tension. Found.	Lit.	% Diff.
1.	Benzene	0.8792	34.86	35.00 ± 0.05	0.40
2.	Bromoform	2.8710	40.70	40.85	0.37
3.	CCl_4	1.5910	45.15	45.00 ± 1.0	0.33
4.	Chlorobenzene	1.1040	37.73	37.41	0.86
5.	Ethyl ether	0.7145	10.92	10.70 ± 0.2	0.18*
6.	Ethylene dibromide	2.1800	36.65	36.54	0.30
7.	*n*-Hexane	0.6814	51.11	51.10	0.02
8.	Methyl-*n*-propyl ketone	0.8110	6.215	6.28	1.04
9.	Nitrobenzene	1.2040	25.80	25.66	0.55
10.	*o* Nitrotoluene	1.1640	27.36	27.19	0.63
11.	*m*-Nitrotoluene	1.1570	27.86	27.68	0.65
12.	Toluene†	0.8606	36.09	36.10	0.03

* The deviation is 0.18% if literature value is taken as 10.90. If the mean value is taken as the basis, the deviation is 2.06%.

† For toluene, the values given are at 25°. Density of distilled water at 25° = 0.9971 g./c c.

TABLE III

Interfacial tension of liquids in contact with water at diff. temp.

	Liquid.	20°.	25°.	30°.	40°.	50°.
1.	Benzene	34.86	34.65	34.48	34.07	33.52
2.	CCl_4	45.24	44.82	44.30	43.19	42.20
3.	Chlorobenzene	37.73	36.86	36.17	35.28	34.36
4.	Ethylene dibromide	36.65	36.08	35.41	34.22	33.12
5.	Methyl-*n*-propyl ketone	6.215	6.805	5.93	5.701	5.45
6.	Toluene	...	35.09	35.68	34.88	34.08

The pipette developed and herein described can be readily prepared and used for the rapid and accurate determination of surface and interfacial tensions of liquids.

DEPARTMENT OF CHEMICAL ENGINEERING,
INDIAN INSTITUTE OF TECHNOLOGY,
KHARAGPUR.

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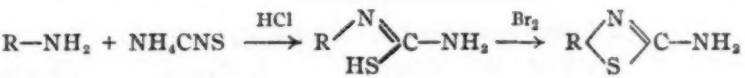
STUDIES ON 2-AMINOBENZTHIAZOLES

By P. N. Bhargava and B. T. Baliga

2-Aminobenzthiazoles have been synthesised by condensing *as*-arylthioureas with bromine in chloroform, and their properties and group reactions leading to various derivatives have been studied.

Hugershoff (*Ber.*, 1903, **36**, 3121) prepared 2-aminobenzthiazoles by the action of liquid bromine on asymmetrical phenylthiourea in chloroform. Hunter *et al.* (*J. Chem. Soc.*, 1925, 2023; 1926, 1385) studied the conditions for the formation of alkyl-substituted 2-aminobenzthiazoles and showed that in these compounds tautomerism was exhibited by the mobility of the symmetrical triad system, as verified by symmetry test (Ingold and Piggot, *ibid.*, 1922, **121**, 2381) and substitution test (Farrow and Ingold, *ibid.*, 1924, **125**, 2543). Kaufmann and Schubert (U. S. P., 1,787,315; 1,787,316) and Kaufmann *et al.* (*Arch. Pharm.*, 1928, **266**, 215) studied substituted 2-aminobenzothiazoles, prepared by the thiocyanation of *para*-substituted aromatic amines in acid solution. Brewster and Dains (*J. Amer. Chem. Soc.*, 1936, **58**, 1364) prepared several thiazoles by the cupric thiocyanate method and found that thiocyanation did not occur in compounds containing acetamido or carbethoxyamino groups. It was therefore considered worthwhile, in view of their medicinal importance as local anaesthetics, to prepare ten 2-aminobenzthiazoles (I) by the method of Hugershoff (*loc cit.*) from ten different *as*-arylthioureas, obtained by the well-known method of De Clermont (*J. Chem. Soc.*, 1877, **31**, 70) and also that of Berkebile and Fries (*J. Chem. Ed.*, 1948, **25**, 618).



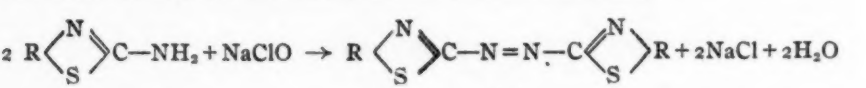
(I)

The $-NH_2$ group in the compounds, being considered full of utility for the preparation of derivatives, has been acetylated and benzoylated in a few cases only, yielding 2-acetylamino- and 2-benzoylamino-benzthiazoles.

The process of diazotisation of the free $-NH_2$ group and subsequent coupling with alkaline β-naphthol to form azo-β-naphthol derivatives have been found to be more difficult with increase in substitution in the benzene nucleus. Thus, only five of the ten thiazoles have yielded well-defined azo-β-naphthol derivatives.

Further, considering from the practical point of view that paper, impregnated with 2-aminobenzthiazoles, is used in legal documents or cheques as safety paper because ink eradicators, which usually contain sodium hypochlorite, develop a red coloured blot almost instantaneously when applied. An attempt has been made to substantiate the course of this reaction with sodium hypochlorite in the case of all

the ten benzthiazoles according to Kirk *et al.* (*J. Org. Chem.*, 1943, **8**, 557), when coloured 2 : 2′-dibenzo-azothiazoles (II) have been obtained.



(II)

These azo compounds exhibit characteristic colour in glacial acetic acid, thus showing the nature of a dye. A confirmation of the constitution of these azo compounds has been corroborated by the results of the estimation of —N=N— group and isolation and identification by the mixed m.p. of the corresponding original 2-aminobenzthiazoles from them by reduction with tin and hydrochloric acid and subsequently adding ammonia till alkaline.

Experimental

2-Aminobenzthiazole.—*as*-Phenylthiourea (10 g.), suspended in dry chloroform (25 c.c.), was gradually treated with liquid bromine (6 c.c.) in dry chloroform (50 c.c.). The mixture was refluxed on a water-bath till no more HBr had evolved. The solid was filtered free of the solvent, dried, suspended in sulphurous acid solution, and sulphur dioxide gas was passed till a clear solution was obtained. It was filtered and treated with ammonia till alkaline. The precipitated 2-aminobenzthiazole was filtered, washed, dried and finally crystallised from hot rectified spirit in a white crystalline form, m.p. 129°, yield 7.5 g.

Similarly other 2-aminobenzthiazoles were prepared. The properties and analytical data are recorded in Table I.

Table I

2-Aminobenzthiazoles.

[B denotes benzthiazoles. A denotes 2-Amino-].

Compounds.	% Yield.	M.P.	Formula.	% Nitrogen. Found.	% Nitrogen. Calc.	% S or halogen. Found.	% S or halogen. Calc.
1. A-B[1]	75	129°	$C_7H_6N_2S$	18.12	18.66	20.98	21.33
2. A-chloro-B	70	202°	$C_7H_5N_2ClS$	15.39	15.18	18.98	19.24
3. A-6-bromo-B[2]	80	212°	$C_7H_5N_2BrS$	12.42	12 24	34.62*	34.90
4. A-*o*-nitro-B[3]	65	161°	$C_7H_5O_2N_3S$	20.98	21.54	15.92*	16.41
5. A-4-methyl-B[2]	75	136°	$C_8H_8N_2S$	17.48	17.08	19 12	19.51
6. A-5-methyl-B	74	143°	$C_8H_8N_2S$	17.52	17.08	19.24	19 51
7. A-6-methoxy-B[4]	70	146°	$C_8H_8ON_2S$	15.28	15.55	16.98	17.77
8. A-6-ethoxy-B[4]	72	173°	$C_9H_{10}ON_2S$	14.08	14.43	15.98	16.49
9. A-α-naphthothiazole[2]	50	250°	$C_{11}H_8N_2S$	13.85	14.00	15.75	16.00
10. A-β-naphthothiazole[2]	70	238°	$C_{11}H_8N_2S$	14.33	14.00	15.62	16.00

* Refers to halogen.

1. Hugershoff, *loc. cit.*
2. Hunter *et al.*, *loc. cit.*, 1926.
3. ,, *loc. cit.*, 1925.
4. ,, *J. Chem. Soc.*, 1927, 1186.

2-Acetylaminobenzthiazole.—2-Aminobenzthiazole (1 g.) was heated under reflux with acetic anhydride (4 c.c.), cooled and poured into water. The precipitate obtained was crystallised from hot water, m.p. 186°.

Similarly the acetyl derivatives of some other thiazoles were prepared. The number of acetyl group in these derivatives was found to be one on analysis. The acetylation was not successful in the case of 2-amino-5-ethoxybenzthiazole, -α-naphthothiazole and -β-naphthothiazole. The properties and analyses are reported in Table II.

2-Benzoylaminobenzthiazole.—2-Aminobenzthiazole was benzoylated as usual into a colorless form, m.p. 184°. Similarly other thiazoles were benzoylated and the number of benzoyl group on analysis was found to be one. The benzoylation was not successful with 2-amino-6-methoxybenzthiazole, -6-ethoxybenzthiazole, -α-naphthothiazole and -β-naphthothiazole. The properties and analytical data are recorded in Table II.

TABLE II

Compounds.	Acetyl derivative.				Benzoyl derivative.			
	M.P.	Formula.	% Nitrogen. Found.	Calc.	M.P.	Formula.	% Nitrogen Found.	Calc.
1.	186°	$C_9H_8ON_2S$*	14.62	14.58	184°	$C_{14}H_{10}ON_2S$*	11.10	11.02
2	289°	$C_9H_7ON_2ClS$	12.40	12.35	286°	$C_{14}H_9ON_2ClS$	9.76	9.70
3.	223°	$C_9H_7ON_2BrS$	10.38	10.33	203°	$C_{14}H_9ON_2BrS$	8.44	8.40
4.	286°	$C_9H_7O_3N_3S$	17.90	17.72	203°	$C_{14}H_9O_3N_3S$	14.88	14.84
5.	252°	$C_{10}H_{10}ON_2S$	13.62	13.59	221°	$C_{15}H_{12}ON_2S$	10.40	10.44
6.	224°	$C_{10}H_{10}ON_2S$	13.52	13.59	206°	$C_{15}H_{12}ON_2S$	10.72	10 44
7.	210°	$C_{10}H_{10}O_2N_2S$	12.69	12.61	...	...	...	...

* Hunter *et al.*, *loc. cit.*, 1926.

N.B. The number corresponds to those in Table I.

Benzthiazole-2-azo-β-naphthol.—2-Aminobenzthiazole (1.5 g.), suspended in HCl (dil., 20 c.c.), was diazotised as usual. The product was coupled with β-naphthol (1.4 g.), dissolved in 5% NaOH solution (8 c.c.). The orange-brown azo compound on extraction with ether and crystallisation in vacuum gave purple-red crystals, m.p. 147°. Similarly four other thiazoles formed 2-azo-β-naphthol derivatives, but diazotisation and coupling with the rest five failed, as recorded in Table III.

TABLE III

*2-Azo-β-naphthol derivatives of No.	Colour.	M.P.	Formula.	% Nitrogen. Found.	Calc.
1.	Purple-red	147°	$C_{17}H_{11}ON_3S$	13.82	13.77
2.	Brownish red	232°	$C_{17}H_{10}ON_3ClS$	12.41	12.37
5.	Red	172°	$C_{18}H_{13}ON_3S$	13.22	13.16
9.	Chocolate	276°	$C_{21}H_{13}ON_3S$	11.89	11.83
10.	Brownish red	192°	$C_{21}H_{13}ON_3S$	11.92	11.83

2 : 2′-*Dibenzo-azothiazole.*—2-Aminobenzthiazole (1 g.) in water (30 c.c.) was gradually treated with 0.3 *N* sodium hypochlorite solution (50 c.c.). The purple

precipitate, produced after being washed with ether, separated from a mixture of chloroform and light petroleum ether (1 : 1) at 20° as dark purple crystals, m.p. 159°. It developed a yellow colour in glacial acetic acid. Similarly other substituted dibenzo-azothiazoles were prepared. The properties and analytical data are mentioned in Table IV.

TABLE IV

[D denotes dibenzo-azothiazole]

Azothiazoles.	Colour.	M.P.	Colour AcOH.	Formula,	% -N=N-. Found.	Calc.
2 :2′-D-	Purple	159°	Yellow	$C_{14}H_8N_4S_2$	9.382	9.461
2 :2′-4 :4′-Dichloro-D	Black	214°	Do	$C_{14}H_6N_4Cl_2S_2$	7.722	7.672
2 :2′-6 :6′-Dibromo-D	Do	290°	Orange	$C_{14}H_6N_4Br_2S_2$	6.202	6 170
2 :2′-6 :6′-Dinitro-D	Brown	142°	Orange-red	$C_{14}H_6O_4N_6S_2$	7.312	7.293
2 :2′-4 :4′-Dimethyl-D	Pink	228°	Red	$C_{16}H_{12}N_4S_2$	8 524	8.644
2 :2′-5 :5′-Dimethyl-D	Brown	174°	Dark red	$C_{16}H_{12}N_4S_2$	8 723	8.644
2 :2′-6 :6′-Dimethoxy-D	Black	122°	Blood-red	$C_{16}H_{12}O_2N_4S_2$	7.872	7.866
2 :2′-6 :6′-Diethoxy-D	Black	136°	Crimson	$C_{18}H_{16}O_2N_4S_2$	7.188	7.293
2 :2′-Di-α-naphtho-	Pink	212°	Violet	$C_{22}H_{12}N_4S_2$	6.982	7.071
2 :2′-Di-β-naphtho-	Black	194°	Red	$C_{22}H_{12}N_4S_2$	7.123	7.071

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ORGANIC CHEMICAL LABORATORY,
COLLEGE OF SCIENCE,
BANARAS HINDU UNIVERSITY, VARANASI-5.

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COMPLEX COMPOUNDS OF STANNIC IODIDE WITH AMINES. PART I

By Sarju Prasad, K. N. Chatterjee and M. H. Rao

Compounds of stannic iodide with primary mono- and diamines have been prepared in benzene medium and their properties studied. It has been found that 4 mols. of a primary monoamine and 2 mols. of a diamine are attached to one mol. of SnI_4.

Persone (Mellor, "A Comprehensive Treatise on Theoretical and Inorganic Chemistry", Vol. VII, 1923) reported the formation of $SnI_4.3NH_3$ and $SnI_4.6NH_3$ by the action of dry ammonia on SnI_4 in CS_2 or ether, but Ephraim and Schmidt (*Ber.*, 1909, **42**, 3856), who used CCl_4, obtained $SnI_4.8NH_3$ and an unstable compound, $SnI_4.18NH_3$.

Werner and Pfeiffer (*Z. anorg. Chem.*, 1898, **17**, 82) prepared the compounds. $SnCl_4.2C_6H_5NH_2$ and $SnBr_4.2C_6H_5NH_2$, by the action of aniline on the respective tin halide, which decomposed at a higher temperature.

Friedmann *et al.* (*ibid.*, 1911, **71**, 97) studied the formation of the compounds $SnI_4.Py_2.3Py$ and $SnCl_4.2Py$, $SnBr_4.2Py$.

Heiber and Wager (*Annalen*, 1925, **444**, 249) obtained the compounds $(NH_2\text{-}ArNH_2)_2.SnX_4$ and $[(NH_2ArNH_2)SnX_4]_2$ by the action of *o*-, *m*- and *p*-phenylenediamine on stannic halide. By the action of benzidine on $SnCl_4$ and $SnBr_4$ he obtained the compounds $SnX_4(NH_2Ar)_2$ and $SnX_4(NH_2Ar)_4$ respectively and concluded that in these compounds one of the inorganic salt was linked by the subsidiary valence bonds to two nitrogen atoms.

Scaglirani (*Atti R. Acad. Lincei*, 1925, *vi*, **1**, 582) prepared the compounds $SnI_4.5C_6H_{12}N_4$ and $SnI_4.4C_6H_{12}N_4.2CHCl_3$ in chloroform medium.

Scaglirani and Monti (*ibid.*, 1926, **4**, 210) studied the action of hexamine on SnI_4 in different non-aqueous media and obtained the compounds $SnI_4.2C_6H_{12}N_4$; $SnBr_4.4C_6H_{12}N_4.C_2H_2Cl_2$; $SnBr_4.C_6H_{12}N_4.CHCl_3$; $SnBr_4.6C_6H_{12}N_4.CHCl_3$. They concluded that according to Werner's theory of co-ordination there was paucity of satisfactory evidence in interpreting the formation of these compounds.

Karanthsis (*Bull. Soc. Chim.*, 1926, *iv*, **39**, 43) prepared the compound $SnI_3.NMe_4$ by dissolving molecular proportions of SnI_2 and Me_4NI in the presence of an excess of HCl. By a similar method he prepared the corresponding compounds $SnI_3.NH_3Ph$ and $SnI_3.NHC_5H_5$, and Dimitrion (*Praktika*, 1929, **4**, 140) isolated the compounds $MeSnI_3.2C_5H_5N$, $SnCl_4.2C_9H_7N$ and $SnBr_4.2C_9H_7N$.

It is evident that practically no work has been done on the formation of compounds of stannic iodide with amines. The present investigation was therefore undertaken with a view to studying the preparation and properties of these compounds.

TABLE I

Amine-SnI_4 compounds.	Colour.	M.P.	% Sn.		% I.		% Org. matter.		% Nitrogen.	
			Found.	Calc.	Found.	Calc.	Found.	Calc.	Found.	Calc.
Mono-amines.										
Aniline, $Sn[4(C_6H_4NH_2)]I_4$	Whitish brown	150°	12.08	11.91	52.40	58.60	35.62	37.23		
o-Toluidine, $Sn[4(CH_3C_6H_4NH_2)]I_4$	Brown	214°	11.34	11.27	47.42	48.16	41.24	40.57	4.90	5.21
m-Toluidine, ,, ,,	Yellow	175°	11.60	11.27	48.25	48.16	40.15	40.57	5.02	5.31
p-Toluidine, ,, ,,	Yellow	180°	11.50	11.27	48.15	48.16	40.35	40.57		
α-Naphthylamine, $Sn[4(C_{10}H_7NH_2)]I_4$	Yellowish brown	220°	9.93	9.91	45.40	42.37	44.66	47.72		
β-Naphthylamine, ,, ,,	Greenish yellow	214°	9.75	9.91	44.30	42.37	45.95	47.72		
o-Anisidine, $Sn[4(CH_3OC_6H_4NH_2)]I_4$	Yellow	151°	10.56	10.62	45.74	45.42	43.70	43.96		
p-Anisidine, ,, ,,	Ash-coloured	148°	10.60	10.62	45.70	45 42	43.70	43.96		
Butylamine, $Sn[4(CH_3CH_2)_2CH_2NH_2)]I_4$	Yellow liquid	250°	13.50	12.95	54.70	55.29	31.80	31.76		
Benzylamine, $Sn[4(C_6H_5CH_2NH_2)]I_4$	Yellow	174°	11.26	11.28	47.99	48.16	40.75	40.56		
o-Phenetidine, $Sn[4(C_2H_5OC_6H_4NH_2)]I_4$	Yellow	165°	10.34	10.13	43.05	43.23	46.61	46.64		
p-Phenetidine, ,, ,,	Pale yellow	164°	10.33	10.13	43.39	43.23	46.28	46.64		
Diamines.										
Ethylenediamine, $Sn[2(CH_2NH_2)_2]I_4$	White	158°	15.84	15.94	67.95	68.01	16.21	16.05		
Dianisidine, $Sn[2(CH_3ONH_2C_6H_3)_2]I_4$	Ash	195°	10.69	10.68	45.62	45.57	43.69	43.75		
o-Tolidine, $Sn[2(CH_3NH_2C_6H_3)_2]I_4$	White	198°	11.27	11.32	48.86	48.34	39 87	40.34	5.03	5 33
Naphthalenediamine, $Sn[2(C_{10}H_6NH_2)_2]I_4$	Reddish brown	169.8°	12.62	12.62	54.70	53.88	32.68	33.50		
p-Phenylenediamine, $Sn[2(NH_2C_6H_4NH_2)]I_4$	Pink	240°	14.37	14.09	62.24	60.27	23.39	25.64		
Benzidine, $Sn[2(NH_2C_6H_4)_2]I_4$	Brown	182°	11.90	11.93	49.10	51.05	39.00	37.02		

All these compounds melt with decomposition.

EXPERIMENTAL

The amine and stannic iodide used were of B.D H. "extra pure" quality. A dilute benzene solution of the amine was added to the stannic iodide solution in benzene with constant shaking till precipitation was complete. The precipitate was filtered and washed till the washings did not produce any precipitate with stannic iodide. It was dried at the room temperature, analysed and its properties were studied. Iodine was estimated as AgI and in as SnO_2. Nitrogen was estimated by Kjeldahl's method in a few cases and for the rest it was obtained by difference. The results are reported in Table I.

DISCUSSION

According to Sidgwick ("Electronic Theory of Valency", 1927) the maximum covalency that tin can exhibit is 8, but usually it is 6. In all the cases studied, four molecules of monoamines and two molecules of a diamine are co-ordinated with one molecule of stannic iodide, and the maximum covalency of 8 is attained.

Almost all the compounds are semicrystalline powder with the exception of the butylamino compound, which is a liquid, having b.p. 250°. These are fairly stable in dry atmosphere, but when exposed to moist air for a long time, these absorb moisture and decompose. These are insoluble in benzene, ether, chloroform and acetone, and are readily soluble in dilute HCl, but decompose into the corresponding amine, hydroxide of tin and sodium iodide, when treated with a dilute NaOH solution.

$$Sn(4Am)I_4 + 4NaOH \rightarrow Sn(OH)_4 + 4NaI + 4Am.$$

It appears that amines attach themselves to the central atom, chelate compound being formed in the case of diamines and can be represented as Sn (4A) I_4 (where A = primary amine) and Sn (2D) I_4 (where D = diamine). The E.A.N. does not assume the inert gas configuration and therefore the compounds are not very stable.

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CHEMICAL LABORATORIES,
BANARAS HINDU UNIVERSITY,
VARANASI-5.

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2 :6-DIARYL-3-ETHOXYCARBONYL-4-PIPERIDONES AND THEIR *N*-METHYL DERIVATIVES

By P. N. Bhargava and I. D. Saxena

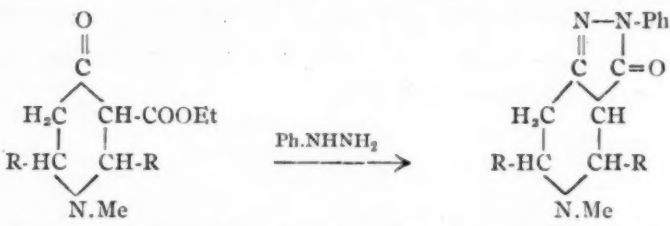
Six new *N*-methyl-2 :6- diaryl-3- ethoxycarbonyl-4-piperidones have been synthesised and converted into pyrazolone derivatives.

Noller *et al.* (*J. Amer. Chem. Soc.*, 1948, **70**, 3853) developed a satisfactory procedure by which they prepared a number of substituted 4-piperidones by condensing ethyl acetoacetate with aromatic aldehydes and ammonium acetate in glacial acetic acid.

The aim of the present investigation was to extend this method in continuation of our earlier work (Bhargava *et al.*, this *Journal*, 1957, **34**, 105) to the synthesis of some new 2 : 6-diaryl-3-ethoxycarbonyl-4-piperidones with a view to converting them into *N*-methyl derivatives of possible therapeutic value as analgesics and antipyretics.

p-Hydroxybenzaldehyde, cinnamaldehyde, *o*-chloro-, *p*-chloro-, *m*-nitro- and *p*-nitro-benzaldehydes, piperonal and 2-hydroxy-1-naphthaldehyde have been employed in the preparation of 2 :6-diaryl-3-ethoxycarbonyl-4-piperidones. The maximum yield of 90% has been obtained in the case of *p*-hydroxybenzaldehyde derivatives and minimum yield of 41% in the case of 2-hydroxy-1-naphthaldehyde derivative. Two of these 4-piperidones have been converted into pyrazolone derivatives.

Condensation with dimethyl sulphate in acetone in the presence of anhydrous potassium carbonate has yielded *N*-methyl-2 :6-diaryl-3-ethoxycarbonyl-4-piperidones and these on treatment with phenylhydrazine have been converted into pyrazolone derivatives, which may show a complex pattern of pharmacodynamic behaviour.



Thus, the structure of *N*-methyl-4-piperidones has been corroborated by the preparation of the characteristic derivatives and analyses.

Experimental

2 :6-Diaryl-3-ethoxycarbonyl -4-piperidones.—A mixture of ethyl acetoacetate (0.25 *M*), aromatic aldehyde (0.5 *M*) and ammonium acetate (0.5 *M*) in glacial acetic acid (35 c.c.) was heated under reflux at 100-150° for 1-2.5 hours. The product was isolated following the procedure of Bhargava *et al.* (*loc. cit.*). The data regarding properties and analyses are recorded in Table I.

TABLE I

No.	Aldehyde condensed.	Yield.**	Solvent of cryst.	Colour.	M.P.	Formula.	%Nitrogen. Found.	Calc.
1.	*p*-Hydroxy-B*	90%	Benzene	White	157°	$C_{26}H_{21}O_5N$	3.86	3.89
2.	Cinnamaldehyde	81	Pet. ether	Pale yellow	126°	$C_{24}H_{23}O_3N$	3.73	3.75
3.	*o*- hloro-B	73	Chloroform	Black	95°	$C_{26}H_{19}O_3NCl_2$	3.52	3.57
4.	*p*-Chloro-B	72	Do	Yellow	180°	$C_{26}H_{19}O_3NCl_2$	3.54	3.57
5.	*m*-Nitro-B	82	Methanol	Yellow	138°	$C_{26}H_{19}O_7N_3$	10.10	10.16
6.	*p*-Nitro-B	79	Acetone	Dirty yellow	110°	$C_{26}H_{19}O_7N_3$	10.08	10.16
7.	Piperonal	84	Pet. ether	Yellow	86°	$C_{27}H_{21}O_7N$	3.42	3.40
8.	2-Hydroxy-1 naphthaldehyde	41	Methanol	Greenish black	191°	$C_{25}H_{25}O_5N$	3.08	3.10

* B denotes benzaldehyde.

** Yield is based on the liberation of 4-piperidones from their hydrochlorides.

1-*Phenyl*-3 : 4-(2' :6'-*diaryl*)-*piperidopyrazolone*-5.— The appropriate piperidone (0.1 *M*) and phenylhydrazine (0.1 *M*) were refluxed in an oil-bath at 125-40° for 1.5-3 hours. After the reaction, the contents were cooled and treated with glacial acetic acid with stirring. The precipitate thus obtained was crystallised from a suitable solvent. The data regarding properties and analyses are mentioned in Table II.

TABLE II

Aldehydes.*	Solvent of cryst.	% Yield.	Colour.	M.P.	Formula.	% Nitrogen. Found.	Calc.
No. 1.	Acetone	54	White	125°	$C_{24}H_{21}O_3N_3$	10.48	10.52
3.	Chloroform	90	Brown	215°	$C_{24}H_{19}ON_3Cl_2$	9.70	9.63

* The number corresponds to the respective aldehydes shown in Table I.

N-*Methyl*-2 :6-*diaryl*-3-*ethoxycarbonyl*-4-*piperidones*.—The piperidone (0.2 *M*) in acetone (25 c.c.), dimethyl sulphate (0.2 *M*) and anhydrous potassium carbonate (0.3 *M*) were refluxed on a water-bath for 3 hours. At the end of the reaction, the contents were poured into ice-cold water (100 c.c.) and stirred well. The precipitate was filtered and crystallised from alcohol. Relevant data are recorded in Table III.

TABLE III

Aldehydes*.	%Yield.	Colour.	M.P.	Formula.	% Nitrogen. Found.	Calc.
No. 1.	82	White	145°	$C_{21}H_{23}O_5N$	3.74	3.79
2.	86	Do	130°	$C_{25}H_{27}O_3N$	3.68	3.65
5.	87	Brick-red	96°	$C_{21}H_{21}O_7N_3$	9.80	9.83
6.	78	Red	116°	$C_{21}H_{21}O_7N_3$	9.85	9.83
7.	69	Yellow	102°	$C_{23}H_{23}O_7N$	3.31	3.29
8.	44	Do	136° (decomp.)	$C_{29}H_{27}O_5N$	3.00	2.99

* The number corresponds to the respective aldehydes shown in Table I.

1-Phenyl-3:4 (N-methyl-2' : 6'-diaryl)-piperido - pyrazolone-5.—The corresponding piperidone (0.1 *M*) and phenylhydrazine (0.1 *M*) were refluxed in an oil-bath at 125-140° for 2-2.5 hours. After the reaction, the contents were cooled and treated with absolute alcohol. Most of the tarry matter dissolved leaving behind greyish white solids. These were filtered and crystallised from suitable solvents. The data regarding properties and analyses are recorded in Table IV.

TABLE IV

Aldehydes.	Refluxed for.	Refluxed at.	% Yield.	Solvent of cryst.	Colour.	M.P.	Formula.	% Nitrogen. Found.	% Nitrogen. Calc.
No. 2.	2.5 hrs.	125°	75	Acetone	White	285° (decomp.)	$C_{19}H_{27}ON_3$	9.63	9.69
3.	2.0	130°	85	Ether-alcohol	Black	170°	$C_{25}H_{21}O_5N_5$	14.90	14.86
7.	2.5	125°	64	Chloroform	Brown	173°	$C_{27}H_{23}O_5N_3$	9.00	8.95
8.	2.5	140°	50	Ether	Black	183°	$C_{33}H_{27}O_3N_3$	8.12	8.18

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ORGANIC CHEMICAL LABORATORY,
COLLEGE OF SCIENCE,
BANARAS HINDU UNIVERSITY,
VARANASI—5.

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SPECTROPHOTOMETRIC STUDIES ON FERROUS COMPLEXES OF QUINOLINE- AND PYRIDINE-CARBOXYLIC ACIDS. PART III. FERROUS DIPICOLINIC ACID AND FERROUS QUINOLINIC ACID SYSTEMS

By Bireswar Banerjee and Priyadaranjan Rây

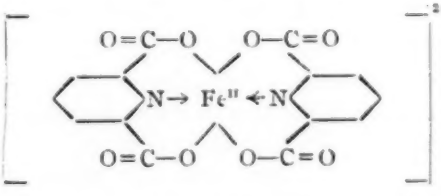
Highly soluble coloured ferrous complexes of dipicolinic and quinolinic acids have been studied by spectrophotometric method. The ferrous complexes of some other pyridine di- and tricarboxylic acids with a carboxyl group in the α-position to the nitrogen atom have also been studied in a qualitative manner.

Ferrous dipicolinic acid complex shows its maximum colour intensity between p_H 5 and 7 and the λ_{max} at 480 mμ. The intensity of colour, however, decreases in the presence of KCN or pyridine. The colour system obeys Beer's law, and its composition is given by 1 Fe^{II} : 2 acid, with an instability constant, 1.85×10^{-7}.

The soluble coloured complex of ferrous quinolinic acid has been found to give its maximum colour intensity between p_H 5.7 and 7.0 with λ_{max} at 420 mμ, and the colour is intensified with the addition of KCN, and to some extent with pyridine. The λ_{max} for cyanide-containing system lies at 440 mμ. The colour system with or without the cyanide obeys Beer's law under specified conditions. The composition of the complex is represented by 1 Fe^{II} : 3 acid with an instability constant of 3.47×10^{-11}.

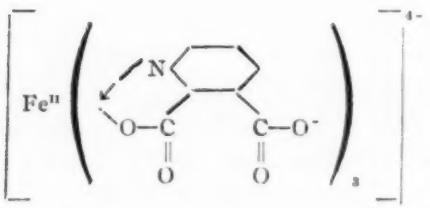
In the previous papers (Parts I and II, this *Journal*, 1958, **35**, 297, 493) the formation of ferrous complexes with quinaldinic acid and picolinic acid has been studied by the spectrophotometric method. The results of studying the ferrous complexes of dipicolinic acid and quinolinic acid and also of other pyridine di- and tricarboxylic acids with at least one carboxyl group at the α-position to the nitrogen atom of the pyridine ring, are reported in the present communication.

The composition of ferrous dipicolinic acid (pyridine-2 : 6-dicarboxylic acid) complex from spectrophotometric measurements, following Job's method, is given by 1 Fe : 2 acid. The complex may therefore be represented by the following configuration, where the acid molecule behaves as a tridentate ligand.



The value of the instability constant of the complex was found to be 1.85×10^{-7}.

Quinolinic acid (pyridine-2 : 3 dicarboxylic acid) was found by Job's method to combine with ferrous ion yielding a complex of the composition 1 Fe : 3 acid. It can therefore possess an octahedral configuration as shown below :



Each acid molecule here behaves as a bidentate ligand with one of its carboxyl group remaining free. The value of the instability constant for the quinolinate complex was found to be 3.47×10^{-11}.

Pyridine-2 : 4- and 2 : 5-dicarboxylic acids and pyridine-2 : 4 : 6-, -2 : 3 : 6- and -2 : 4 : 5-tricarboxylic acids have all been found to furnish yellow to red ferrous complexes. Like ferrous quinaldinate and picolinate, the colour of the ferrous complexes of all the above mentioned pyridine carboxylic acids, with the exception of those of dipicolinic acid (2 : 6) and collidinic acid (2 : 4 : 6), is highly intensified by the addition of potassium cyanide solution and also to a considerable extent by pyridine. As in the case of picolinic acid, the part played by potassium cyanide in intensifying the colour of the soluble ferrous complex possibly lies in the formation of a cyano complex in which a molecule of the pyridine di- or tri-carboxylic acid in their coloured complexes is replaced by an equivalent number of cyanogen groups. They, thus, form anionic complexes, the colour intensity of which increases with an increasing amount of KCN and then finally reaches to a constant maximum value. In all these cases the absorption maximum remains practically unaltered.

It is, however, of striking interest to note that in the cases of dipicolinic acid and collidinic acid, the colour of the ferrous complex, in contrast to the behaviour of the ferrous complexes of other pyridine carboxylic acids, is considerably reduced in intensity by the addition of an excess of potassium cyanide.

EXPERIMENTAL

A Unicam SP 600 spectrophotometer and a Cambridge Bench Type p_H meter were used in this work. The reagents used were all of guaranteed quality.

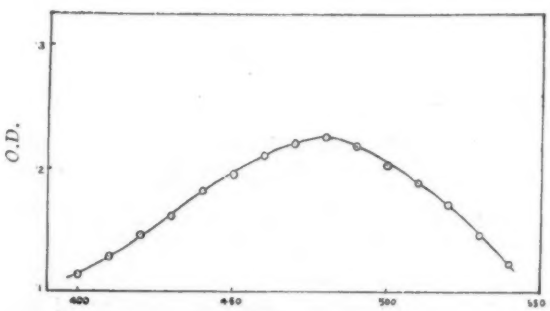
Dipicolinic, quinolinic, collidinic and pyridine-2 : 3 : 6-tricarboxylic acids were prepared by the permanganate oxidation of 2 : 6-dimethylpyridine, quinoline, collidine, and quinaldinic acid respectively (Ladenburg and Roth, *Ber.*, 1885, **18**, 52; Königs, *Ber.*, 1879, **12**, 983; Voigt, *Annalen*, 1885, **228**, 31; Miller, *Ber.*, 1891, **24**, 1916). Lutidinic and *iso*cinchomeronic acids were prepared by the permanganate oxidation of a mixture of 2 : 4- and 2 : 5-dimethylpyridine and then by subsequent separation of the two acids (Banerjee and Rây, this *Journal*, 1957, **34**, 208). Pyridine-2 : 4 : 5-tricarboxylic acid was prepared by the oxidation of berberine with nitric acid (Weidel, *Ber.*, 1879, **12**, 410).

Ferrous Dipicolinic Acid System

With dipicolinic acid iron (II) forms a highly soluble yellow coloured complex with its absorption maximum lying in the region of 480 mμ. The optimum p_H for the maximum colour formation ranges between 5 and 7. Unlike picolinic or quinaldinic acid and some other pyridine carboxylic acids, the colour intensity of the dipicolinic acid complex diminishes with the addition of potassium cyanide or pyridine. The maximum colour formation also requires some time, at least a period of 30 minutes at p_H 6.4 and above. The colour is quite stable and remains unchanged for 24 hours at room temperature. At least one and half times the theoretical quantity of dipicolinic acid is required for the maximum development of colour. The coloured complex obeys Beer's law and the sensitivity is given by 0.044γFe/cm² (Sandell, "Colorimetric Determination of Traces of Metals", Interscience Publishers, New York, 1950, p. 47).

Wave-length of Absorption Maximum (λ_{max}).—The same procedure, as described before (cf. Part I, *loc. cit.*), was followed. The reagent and the Fe^{II} blank separately showed practically no absorption within the range of measurement. Fig. 1 shows the optical density values of the coloured complex at different wave-lengths. It should be noted that all measurements were made after one hour since the time of mixing the solution, when the colour was fully developed. From Fig. 1, it can be concluded that λ_{max} for ferrous dipicolinic acid system lies at 480 mμ.

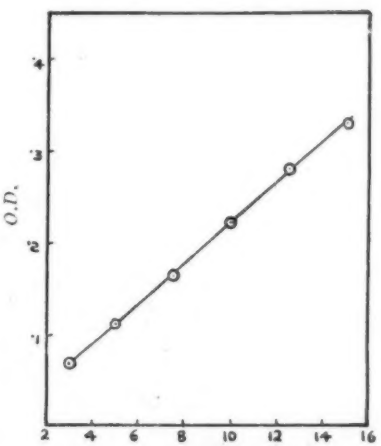
FIG. 1



Wave-length (mμ).

Ferric nitrate (50 p.p.m.) 10 c.c.
$NH_2OH.HCl$ (5%), 5 c.c.
Dipicolinic acid (0.25%), 10 c.c.
Total volume, 50 c.c.
Cell used, 1 cm. p_H, 6.

FIG. 2



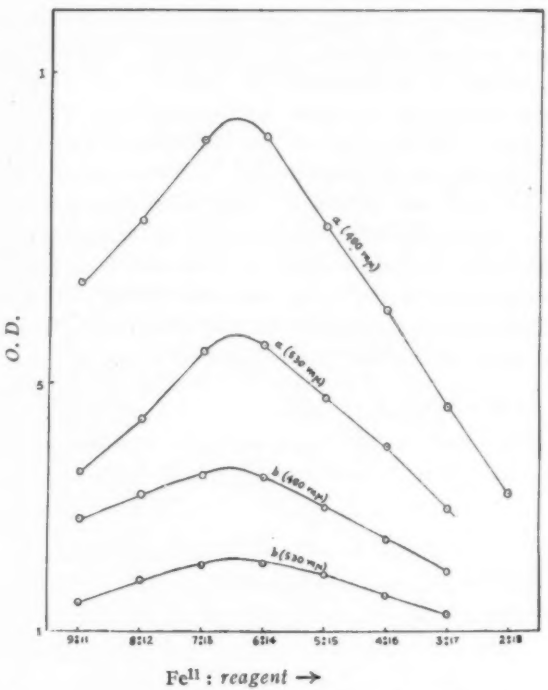
Fe (*p.p.m.*).

Ferric nitrate (50 p.p.m. Fe), *x* c.c.
$NH_2OH.HCl$ (5%), 5 c.c.
Dipicolinic acid (0.25%), 10 c.c.
Total vol., 50 c.c.
Cell used, 1 cm. 480 mμ. p_H, 6.

Beer's Law.—The coloured complex obeys Beer's law. This is evident from the optical density values shown in Fig 2.

Composition of the Coloured Complex of Ferrous Iron and Dipicolinic Acid.—The composition of the coloured complex was determined by Job's method at p_H 5.99 as in the case of ferrous picolinic acid system. The results of measurements are shown in Fig. 3 (a, b). It is clear that the composition of the complex is represented by 1 Fe : 2 acid.

FIG. 3



(a) Ferrous amm. sulphate (0.005*M*) containing $NH_2OH.HCl$ (1%), *x* c.c. Dipicolinic acid (0.005*M*), *y* c.c. KNO_3 (1*M*), 10 c.c. (added to maintain constant ionic strength). Buffer (5.99 p_H), 18 c.c. Total volume, 50 c.c. Cell used, 2 cm.
(b) Ferrous amm. sulphate (0.002*M*) containing $NH_2OH.HCl$ (1%), *x* c.c. Dipicolinic acid (0.002*M*), *y* c.c. All the other conditions are exactly the same as for (a).

Instability Constant of the Coloured Complex.—The instability constant of the coloured complex can be derived as in the previous cases from its dissociation in solution according to the equation :

$$(FeDip_2)^{2-} \rightleftharpoons Fe^{2+} + 2\ Dip^{2-}$$

$$K_c = \frac{[Fe^{2+}] \times [Dip^{2-}]^2}{[(FeDip_2)^{2-}]}$$

where H_2Dip = one molecule of dipicolinic acid. The values of Dip^{2-} and K_c are calculated as in the case of the quinaldinic acid complex.

$$K_s = \frac{[Fe^{2+}]}{[(FeDip_2)^{2-}]} \times \frac{K^2_{a_2}\{[Dip_t] - 2[(FeDip_2)^{2-}]\}^2}{\{K_{a_2} + [H^+]\}^2} \quad \ldots \quad (1)$$

The symbols have the same significance as in previous parts. K_{a_2}, the dissociation constant of $(HDip)^-$, was determined at 30°, following the method suggested by Bjerrum ("Metal-ammine Formation in Aqueous Solutions", P. Haase and Son, Copenhagen, 1941).

Dissociation Constant of Dipicolinic Acid

The method of its determination consists in the titration of a solution of dipicolinic acid with a standard (carbonate free) alkali and noting the p_H values of the solution after each addition of the latter.

The dissociation of a dicarboxylic acid may be represented as follows:

$$H_2A \rightleftharpoons H^+ + (HA)^- \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

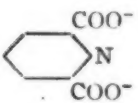
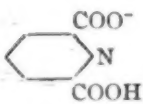
$$(HA)^- \rightleftharpoons H^+ + A^{2-} \quad \ldots \quad \ldots \quad \ldots \quad (3)$$

where H_2A represents a molecule of the dicarboxylic acid. Now for the successive acid dissociation constants we get

$$K_{a_1} = \frac{[HA^-] \times [H^+]}{[H_2A]} \quad \ldots \quad \ldots \quad (4)$$

and

$$K_{a_2} = \frac{[A^{2-}] \times [H^+]}{[HA^-]} \quad \ldots \quad \ldots \quad \ldots \quad (5)$$

where A^{2-} =  and $(HA)^-$ = 

Let B be the total molar concentration of dipicolinic acid taken, so that

$$B = B_0 + B_1 + B_2 \quad \ldots \quad \ldots \quad \ldots \quad (6)$$

where B_0, B_1 and B_2 are the respective molar concentration of Dip^{2-}, $HDip^-$ and H_2Dip; and let P be the molar concentration of the alkali added. Then from the measurements of the p_H of the solution we get,

$$2B - 2B_2 - B_1 - H^+ = P - OH^- \quad \ldots \quad \ldots \quad (7)$$

(Acid neutralised) (Alkali used up)

which on transposition gives

$$2B_2 + B_1 = 2B - P - H^+ + OH^- \quad \ldots \quad \ldots \quad (8)$$

As it is a case of stepwise dissociation, where the amount of acid neutralised is assumed to be less than B, the process (2) may be regarded as still incomplete, and so the amount of B_0 formed is negligibly small and can be ignored. Then from the equation (6) we get,

$$B = B_1 + B_2 \quad \ldots \quad \ldots \quad \ldots \quad (9)$$

Substituting this value of B in (7) we get,

$$B_1 = P + H^+ - OH^- \quad \ldots \quad \ldots \quad \ldots \quad (10)$$

and hence,

$$B_2 = B - P - H^+ + OH^- \quad \ldots \quad \ldots \quad (11)$$

So,

$$K_{a_1} = \frac{B_1 \times [H^+]}{B_2} = \frac{[P + H^+ - OH^-] \times [H^+]}{[B - P - H^+ + OH^-]} \quad \ldots \quad (12)$$

Again, when the acid neutralised is more than B, process (2) can then be regarded as complete, and so B_2 may be taken as negligibly small. Then from (6) we get

$$B = B_0 + B_1 \quad \ldots \quad \ldots \quad \ldots \quad (13)$$

and from (7) we get

$$B_1 = 2B - P - H^+ + OH^-$$

Hence,

$$B_0 = P - B + H^+ - OH^- \quad \ldots \quad \ldots \quad (14)$$

Therefore,

$$K_{a_2} = \frac{B_0 \times [H^+]}{B_1}$$

$$= \frac{[P - B + H^+ - OH^-] \times [H^+]}{[2B - P - H^+ + OH^-]} \quad \ldots \quad (15)$$

The formation curves for these systems were obtained by plotting $\bar{\eta}$ against p_H values for each separate observations ; where $\bar{\eta}$ = average number of hydrogen ions bound to a fully dissociated ligand anion, *i.e.*,

$$\bar{\eta} = \frac{\text{Total No. of } H^+ \text{ bound}}{\text{Total No. of ligand molecules present}}$$

$$= \frac{2B_2 + B_1}{B}.$$

It will be clear from equations (4) and (5) that when $\bar{\eta} = 0.5$ and 1.5 respectively, K_{a_2} and K_{a_1} become equal to the corresponding $[H^+]$ value. Hence, by plotting the value of $\bar{\eta}$ against p_H, the values of K_{a_2} and K_{a_1} can be readily obtained.

The results of measurements are recorded in Table I, and the $\bar{\eta}/p_H$ curve is plotted in Fig. 4.

TABLE I

Acid taken = 150 c.c. of 0.004*M*. Alkali = 0.0999*N*-NaOH. Temp. = 30°.

B (conc. of the acid in moles/litre).	Alkali added.	$2B_2 + B_1 + H^+$.	p_H.	$\frac{2B_2 + B_1}{B} = \eta$.
0.00397	1 c.c.	0.00728	2.66	1.28
0.00395	2	0.00658	2.78	1.24
0.003922	3	0.00588	2.93	1.20
0.003896	4	0.00519	3.10	1.13
0.003872	5	0.00454	3.41	1.07
0.003847	6	0.00385	3.91	0.96
0.003822	7	0.00319	4.39	0.82
0.003797	8	0.00255	4.73	0.67
0.003774	9	0.00189	5.01	0.499
0.003751	10	0.00126	5.32	0.33
0.003727	11	0.000634	5.78	0.17

From Fig. 4, K_{a_2} corresponding to $\bar{\eta} = 0.5$ was found to be 1×10^{-5}. As the instability constant of ferrous dipicolinic acid complex had to be determined at about p_H 6 it was assumed that the process (2) for the dissociation of the acid might be regarded as complete. Therefore the value K_{a_2} only was necessary for the calculation of the instability constant of the ferrous dipicolinic acid complex.

FIG. 4

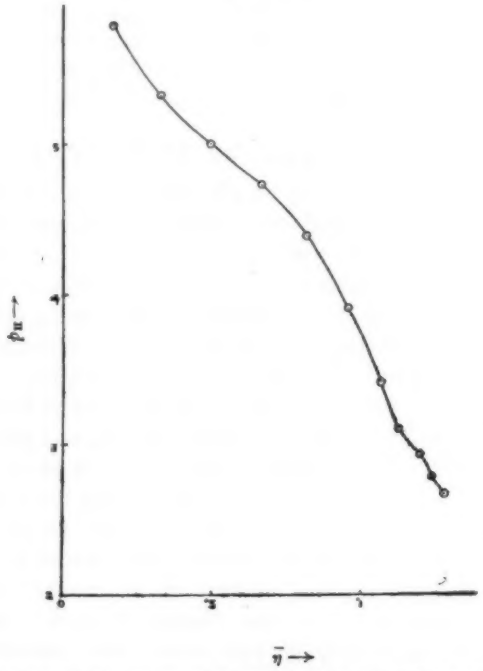


Table II (A, B) records the measured optical density values of the coloured complex in equilibrium.

TABLE II

A. Ferrous amm. sulphate (0.002M) containing $NH_2OH.HCl$ (1%) = x c.c.
Dipicolinic acid (0.005M) = y c.c. KNO_3 (1 M) soln. = 10 c.c.
Buffer = 18 c.c. (p_H 5.99). Cell = 2 cm. 480 mμ.

Dipicolinic acid (c.c) ...	1	2	3(a)	4	5(b)	6	7(c)	8(d)	9
Fe soln. (c.c.) ...	9	8	7	6	5	4	3	2	1
O.D. ...	0.040	0.072	0.118	0.176	0.223	0.229	0.184	0.124	0.070

B. Ferrous amm. sulphate (0.002M) containing $NH_2OH.HCl$ (1%) = x c.c.
Dipicolinic acid (0.004M) = y c.c. All the other conditions are exactly the same as in A.

Dipicolinic acid (c.c.) ...	4	6(e)	8	10(f)	12	14(g)	16
Fe soln. (c.c) ...	16	14	12	10	8	6	4
O.D. ...	0.172	0.279	0.411	0.525	0.476	0.378	0.240

From equation (1) K_e was calculated for a, b, c, d, e, f, g. The results are recorded in Table III.

TABLE III

$K_{a_2} = 1 \times 10^{-5}$. $[H^+] = 0.1023 \times 10^{-5}$.

No.	[Dip]	[FeDip$_2$]	[Fe^{2+}]	K_e
a	3.00×10^{-4}	4.76×10^{-5}	2.32×10^{-4}	1.68×10^{7}
b	5.00×10^{-4}	8.99×10^{-5}	1.10×10^{-4}	1.03×10^{-7}
c	7.00×10^{-4}	7.42×10^{-5}	4.58×10^{-5}	1.55×10^{-7}
d	8.00×10^{-4}	5.00×10^{-5}	3.00×10^{-5}	2.42×10^{-7}
e	4.80×10^{-4}	1.13×10^{-4}	4.47×10^{-4}	2.10×10^{-7}
f	8.00×10^{-4}	2.12×10^{-4}	1.88×10^{-4}	1.03×10^{-7}
g	1.12×10^{-3}	1.52×10^{-4}	8.80×10^{-5}	3.18×10^{-7}

Hence K_e (mean) $= 1.85 \times 10^{-7}$

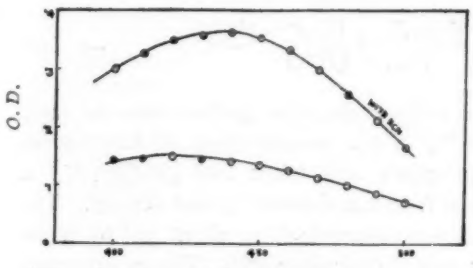
Ferrous Quinolinic Acid System

With quinolinic acid iron (II), as already stated, forms a highly soluble coloured complex. The colour is intensified with the addition of potassium cyanide or pyridine as is the case with ferrous picolinic acid and quinaldinic acid complexes. It resembles particularly the picolinic acid complex in this respect. There is, however, one difference namely, that it takes some time for the maximum colour development at a p_H higher than 6, or with a high concentration of KCN or pyridine. When optical densities were measured after the same interval of time for different solutions, a region of maximum intensification was observed with a moderate concentration of KCN. The λ_{max} of the simple ferrous quinolinic acid complex lies between 410 mμ and 430 mμ, and that of the cyanide-containing system at a somewhat higher value of 440 mμ. As in the case of picolinic acid, with the addition of a large excess of pyridine the λ_{max} shifts towards the ultraviolet region. The sensitivity of the simple coloured system is given by 0.066γ (Sandell, *loc. cit.*) and that of the cyanide-containing system by 0.028γ Fe/cm^2. At least six times the theoretically required amount of the reagent is necessary for the maximum colour development. For the cyanide-containing system, as large as 100 moles of the latter for each mole of iron present are required for the maximum colour formation. The optimum p_H for colour formation lies between 5.7 and 7.0.

At about p_H 8, the colour of the simple ferrous quinolinic acid system is somewhat weaker and assumes a reddish tint. At a higher p_H turbidity sets in. The colour system with or without the potassium cyanide under specified conditions obeys Beer's law and is quite stable at room temperature for 24 hours.

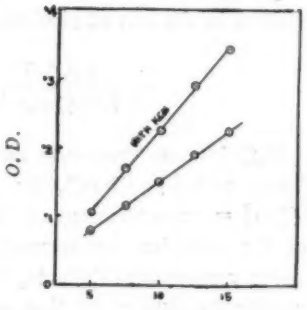
Wave-length of Absorption Maximum.—The same procedure as in the case of ferrous quinaldinic acid system was followed. The reagent blank (without iron) showed negligible absorption at about 420 mμ. Fig. 5 shows the optical density values of the coloured complex at different wave-lengths with or without KCN. It should be noted that in this case all measurements were made after one hour since the time of mixing the solutions. During this period it was found necessary to shake the mixture repeatedly to facilitate the development of colour. The mixture was found to show a strong tendency for bubble formation. Care had therefore to be taken to eliminate these before making the measurements. From Fig. 5 it can be concluded that λ_{max} for the simple ferrous quinolinic acid system lies between 410 and 430 mμ and that of the cyanide-containing system at 440 mμ.

FIG. 5



Ferric nitrate (50 p.p.m. Fe), 10 c.c. $NH_2OH.HCl$ (5%), 5 c.c. Quinolinic acid (0.4%), 10 c.c. KCN (2%), 15 c.c. Total vol., 50 c.c. Cell, 1 cm. p_H, 6.0 (without KCN) and p_H, 6.6 (with KCN).

FIG. 6

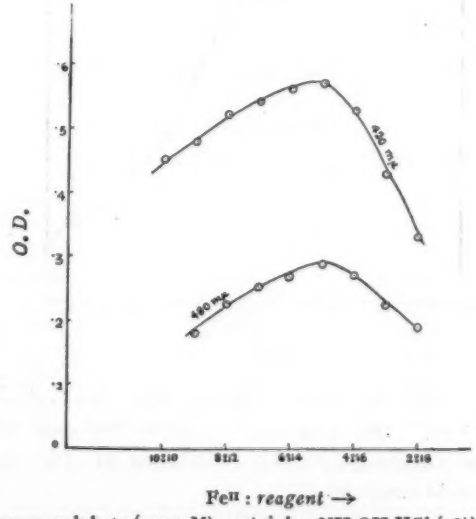


Ferric nitrate (50 p.p.m. Fe), x c.c. $NH_2OH.HCl$ (5%), 5 c.c. Quinolinic acid (0.4%), 10 c.c. Total vol., 50 c.c. Cell, 1 cm. KCN (2%), 15 c.c.. p_H, 6.5 (with or without KCN). mμ, 420 (without KCN)and 440 (with KCN).

Beer's Law.—The coloured complex with or without cyanide obeys Beer's law in the p_H range of 5.7 to 7.0. Fig. 6 gives a graphical representation of the optical density values for Beer's law.

Composition of the Coloured Complex of Fe^{II} *and Quinolinic Acid.*—The composition of the coloured complex was determined spectrophotometrically by Job's method at p_H 5.99 as before. The values of measurements are represented in Fig. 7. It is thus clear that the composition of the coloured complex is given by 1 Fe : 3 acid.

FIG. 7



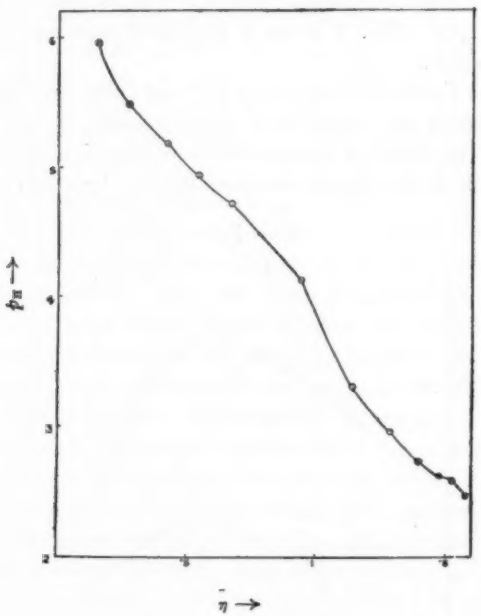
Ferrous ammo. sulphate (0.005 *M*) containing $NH_2OH.HCl$ (1%), x c.c. Quinolinic acid (0.005 *M*), y c.c. KNO_3 (1 *M*) 10 c.c. Buffer (5.99 p_H), 28 c.c. Total volume, 50 c.c. Cell, 2 cm.

Instability Constant of the Coloured Complex.—The instability constant of the coloured complex can be derived as in the previous cases. The value of K_c was calculated as in the case of picolinic acid (Part I, *loc. cit.*) from the equation :

$$K_c = \frac{[Fe^{2+}]}{[(FeQui_3)^{-4}]} \times \frac{K_{a_2}^3 \{[Qui_4] - 3\ [(FeQui_3)^{4-}]\}^3}{\{K_{a_2} + [H^+]\}^3} \quad \ldots \quad (16)$$

where H_2Qui = one molecule of quinolinic acid and the other symbols have the same significance as before (Part I, *loc. cit.*). $[Fe^{2+}]$ is the concentration of free ferrous ion, $[Qui_4]$ = concentration of the total quinolinic acid taken and $[(FeQui_3)^{4-}]$ is that of the complex ion formed as calculated from the observed optical density. The dissociation constants of the acid, K_{a_1} and K_{a_2} were determined at about 30° by a set of experiments similar to that made in the case of dipicolinic acid. The experimental results are recorded in Table IV and the $\bar{\eta}/p_H$ curve is represented by Fig. 8.

FG. 8



From Fig. 8, K_{a_1} and K_{a_2} were obtained from the values of $\bar{\eta} = 1.5$ and 0.5 respectively as 2.5×10^{-3} and 1.04×10^{-5}. As in the case of dipicolinic acid, the value K_{a_2} only was necessary for the calculation of the instability constant of the ferrous quinolinic acid complex.

Table V (A, B) record the measured optical density values of the coloured complex in equilibrium.

TABLE IV

Quinolinic acid taken = 150 c.c. of 0.01*M*. Alkali = 0.0999*N* – NaOH. Temp. = 30°.

B (conc. of the acid in moles/litre).	Alkali added.	$2B_2 + B_1 + H^+$.	p_H.	$\frac{2B_2 + B_1}{B} = \bar{n}$.
0.009933	1 c.c.	0.019206	2.46	1.58
0.009804	3	0.017648	2.58	1.53
0.009740	4	0.016880	2.61	1.48
0.009616	6	0.015390	2.73	1.38
0.009434	9	0.013214	2.96	1.28
0.009260	12	0.011120	3.30	1.14
0.009036	16	0.008443	4.12	0.93
0.008824	20	0.005898	4.71	0.67
0.008722	22	0.004674	4.93	0.54
0.008622	24	0.003474	5.18	0.42
0.008523	26	0.002346	5.47	0.27
0.008428	28	0.001146	5.95	0.14

TABLE V

A. Ferrous amm. sulphate (0.002 *M*) containing $NH_2OH.HCl$ (1%) = *x* c.c. Quinolinic acid (0.005 *M*) = *y* c.c. KNO_3 (1 *M*) soln. = 10 c.c. Buffer (p_H 5.99) = 18 c.c. Cell, 2 cm.

Quinolinic acid (c.c.) ...	1	2	3	4(a)	5(b)	6(c)	7(d)	8	9
Fe soln. (c.c.) ...	9	8	7	6	5	4	3	2	1
O.D. (420 mμ) ...	0.033	0.070	0.096	0.122	0.144	0.123	0.120	0.097	0.041

B. Ferrous amm. sulphate (0.001 *M*) containing $NH_2OH.HCl$ (1%) = *x* c.c. Quinolinic acid (0.004 *M*) = *y* c.c. Other conditions are the same as in A.

Quinolinic acid (c.c.) ...	6	8	10(e)	12(f)	14	16 (g)
Fe soln (c.c.) ...	14	12	10	8	6	4
O. D. (420 mμ) ...	0.167	0.196	0.212	0.195	0.168	0.132

From equation (16) K_e was calculated for a,b,c,d,e,f,g. The results are recorded in Table VI.

TABLE VI

$K_{n_2} = 1.04 \times 10^{-5}$. $[H^+] = 0.1023 \times 10^{-5}$.

No.	$[Quin^-]$.	$[FeQuin_3]$.	$[Fe^{III}]$.	K_e.
a	4.00×10^{-4}	7.28×10^{-5}	1.67×10^{-4}	1.04×10^{-11}
b	5.00×10^{-4}	8.60×10^{-5}	1.14×10^{-4}	1.42×10^{-11}
c	6.00×10^{-4}	7.34×10^{-5}	8.66×10^{-5}	4.88×10^{-11}
d	7.00×10^{-4}	7.16×10^{-5}	4.84×10^{-5}	5.84×10^{-11}
e	8.00×10^{-4}	1.27×19^{-4}	7.30×10^{-5}	3.20×10^{-11}
f	9.60×10^{-4}	1.16×10^{-4}	4.40×10^{-5}	6.58×10^{-11}
g	1.28×10^{-3}	7.88×10^{-5}	1.20×10^{-5}	1.31×10^{-11}

Hence, K_e (mean) = 3.47×10^{-11}.

Coloured Systems of Ferrous Complexes with Some Other Pyridine Carboxylic Acids (Di and Tri)

Two other pyridine dicarboxylic acids with -COOH group in the α-position, namely, lutidinic (2 : 4) and *iso*cinchomeronic (2 : 5) acids have been found, as already

stated, to give an intense yellow colour with ferrous ion with λ_{max} in the range of 410 mμ to 440 mμ. The optimum p_H for maximum colour development lies at or about 6 for both. The colour of the ferrous complex of both the acids is intensified by the addition of KCN and pyridine. The sensitivity for both the coloured complexes was found to be almost equal and is given by 0.166γ Fe/cm² without KCN and 0.070γ Fe/cm² with KCN.

The yellow to red ferrous complexes formed in solution by the three pyridine tricarboxylic acids, viz., collidinic acid (2 : 4 : 6), berberonic acid (2 : 4 : 5) and the 2 : 3 : 6-acid, show an absorption maximum at 525mμ for collidinic acid, and at 410 mμ—420 mμ for pyridine 2 : 3 : 6-tricarboxylic acid. The colour of berberonic acid ferrous complex is developed only in strong solutions. This acid has therefore little value for the colorimetric test of iron. The optimum p_H for colour development for these tricarboxylic acids also lies at or about 6. Sensitivity for ferrous collidinic acid complex is given by 0.052γ Fe/cm². It behaves like ferrous dipicolinic acid complex towards KCN and pyridine, which decrease its colour intensity in solution. Pyridine-2 : 3 : 6-tricarboxylic acid ferrous complex, on the other hand, behaves like quinolinic acid with its colour being intensified by the addition of KCN or pyridine. The sensitivity of the coloured complex is 0.09 γ Fe/cm² without KCN and 0.03 γ Fe/cm² with KCN.

Conclusion

Table VII summarises the optimum conditions for colour development as also the sensitivity of coloured ferrous complexes of the quinoline carboxylic acid and of all the pyridine carboxylic acids studied in this series of communication. The instability constants of the coloured complexes have also been furnished for cases specially studied.

Table VII

p_H=6 (in all cases)

Acid.	λ_{max}.	Sensitivity* in γ/cm² (Fe). Without KCN.	With KCN.	Instability constant.
Quinaldinic	500-515 mμ	0.036	0.0096	3.63×10^{-6}
Picolinic	440	0.056	0.0280	5.07×10^{-12}
Dipicolinic	480	0.044	Diminishes	1.85×10^{-7}
Quinolinic	420-440	0.066	0.0280	3.47×10^{-11}
Lutidinic	410-440	0.166	0.070	...
*iso*Cinchomeronic	410-440	0.166	0.0700	...
Collidinic	525	0.052	Diminishes	...
Pyridine-2 : 3 : 6-tricarboxylic	410-420	0.090	0.0300	...

* Sandell, *loc. cit.*

The coloured ferrous complexes of the pyridine carboxylic acids with the exception of those of dipicolinic and collidinic acids show their maximum absorption practically in the same region of the visible spectrum, viz., 410-440 mμ. The absorption is shifted somewhat to the longer wave-length region in the cases of dipicolinic and collidinic acids, resembling that of quinaldinic acid. Of all the

acids, quinaldinic acid serves as the most sensitive reagent for ferrous iron, particularly with KCN. Their relative sensitivity and stability can be represented as follows in an increasing order :

Sensitivity (without KCN) : Lutidinic = *iso*cinchomeronic < pyridine-2:3:6 (acid) < quinolinic < picolinic < collidinic < dipicolinic < quinaldinic acid.

Stability : Quinaldinic < dipicolinic < quinolinic < picolinic acid.

For colorimetric analysis of iron, quinaldinic acid may therefore be regarded as a very useful reagent. The only drawback is that, on account of its high instability constant, a very large excess (25 times the theoretical amount) of the reagent is required for the purpose of estimation. While dipicolinic acid, which comes next in order of sensitivity when used without KCN, cannot be used in presence of KCN, and hence loses its usefulness as a colorimetric reagent. From a consideration of both sensitivity and stability, picolinic acid may also be regarded as a quite useful reagent for the estimation of iron, next in importance to quinaldinic acid. So far as the interference by foreign ions in the case of these two reagents is concerned, there is very little to choose between them (Rây and Bose, *Z. anal. Chem.*, 1933, **95**, 400 ; Majumdar and Sen· this *Journal*, 1950, **27**, 245 ; *Anal. Chim. Acta*, 1953, **8**, 369).

Department of Inorganic Chemistry,
Indian Association for the Cultivation
of Science, Calcutta-32.

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CONDUCTOMETRIC STUDIES ON SILVER TUNGSTATES

By C. M. Gupta and R. S. Saxena

When $AgNO_3$ is added to Na_2WO_4, various silver tungstates are formed, depending on the p_H of the medium. Normal silver tungstate, $Ag_2O.WO_3$, is formed at p_H 8-10. From weakly acid solutions of p_H 5.5 to 7.0 silver ditungstate, $Ag_2O\ 2WO_3$ is obtained. Silver metatungstate having the composition $Ag_2O.4WO_3$ is formed from acid solutions at p_H 4 to 5.

Meagre references are available in literature to the study of the reaction between $AgNO_3$ and Na_2WO_4 at different p_Hs of the solution. Normal silver tungstate was prepared by Zettnow *et al.* (*Ber.*, 1891, **24**, 2930) by treating a normal sodium tungstate with $AgNO_3$. Rosenheim and Kohn (*Z. anorg. Chem.*, 1911, **69**, 247) and Copaux (*Ann. chim. phys.*, 1909, **17**, 217; 1912, **25**, 22) prepared various insoluble salts by double decomposition and they pointed out that metatungstates had the structure of heteropoly acids. There is, however, hardly any reference to the study of this reaction at different p_Hs of the solution by physicochemical methods. In the absence of any detailed study of these silver tungstates, it was considered worth while to investigate these silver complexes at different H^+-ion concentrations of the medium by electrometric methods, so as to obtain more conclusive evidences on their composition. In the present paper, only the results of conductometric titrations have been included and discussed.

Experimental

Merck's guaranteed extra pure reagents, $AgNO_3$ and Na_2WO_4, were used. Air-free conductivity water was used for the preparation of standard solutions and further dilutions. Sodium tungstate was estimated as barium tungstate (Vogel, "A Text Book of Quantitative Analysis, 1953, p. 492). The conductivities were measured by the Kohlrausch Universal Bridge (W. G. Pye, Ltd.). The alternating current was supplied by a low frequency oscillator (1000 c/s) and the point of balance was indicated by minima of sound in the head phone. The titration cell was immersed in an electrically maintained thermostat. The conductance obtained after each addition was corrected for the dilution effect by multiplying the observed conductance by V/X, where V refers to total volume of the solution and X c.c. is the volume of the reactant already taken in the cell (Davies, "Conductivity of Solutions", p. 238). The curves were plotted between the corrected conductance, thus obtained, and the volume of the titrant, using different concentrations of the reactants. The titrations were carried out by both direct and reverse methods (*i.e.*, when Na_2WO_4 solution from the micro-burette was added to $AgNO_3$ solution in the conductivity cell and *vice versa*). Titrations were also performed in varying concentrations of alcohol; 20 c.c. of the reagent was taken in the cell each time (Table I).

TABLE I

Molarity of Na_2WO_4.	Molarity of $AgNO_3$.	Points showing breaks in Aqueous soln. Calc.	Obs.	Alcoholic soln. Calc.	Obs.	Formula supported.
Direct titrations (Fig. 1). p_H = 8–8.5.						
0.0333 *M*	0.01 *M*	3.0 c.c.	2.85 c.c.	2.7 c.c.	2.65 in 10% alc.	
				2.4	2.4 in 20% alc.	
Reverse titrations (Fig. 2). p_H = 8-8.5						$Ag_2O.WO_3$
0.05	0.5	4.0	3.90	3.6	3.50 in 10% alc.	
				3.2	3.20 in 20% alc.	
Titrations in presence of acids (Fig. 3). p_H = 6.						
0.225	0.2	2.5	2.45	2.25	2.2 in 10% alc.	
				2.00	2.0 in 20% alc.	$Ag_2O.2WO_3$
				p_H = 4.6 (Fig. 4).		
0.5	0.2	2.5	2.40	2.25	2.20 in 10% alc.	
				2.00	2.00 in 20 % alc.	$Ag_2O.4WO_3$

DISCUSSION

$AgNO_3$ was found to have p_H 5.6-5.9. The p_H of the Na_2WO_4 was 9.4 and, hence, in solution it behaved strongly alkaline. In alkaline solution only the species WO_4^{2-} ion is said to exist (Emeleus and Anderson, "Modern Aspects of Inorganic Chemistry", 1952, p. 212). This is confirmed by the formation of normal silver tungstate, $Ag_2O.WO_3$, in the alkaline range.

It will be observed from conductometric titration curves in Fig. 2 and the summary of observations in Table I, that one sharp point of intersection is obtained corresponding to the formation of normal silver tungstate, having the composition $Ag_2O.WO_3$ from p_H range of 8 to 10. In direct titrations, Ag_2WO_4 is precipitated and $NaNO_3$ is formed. Since the ionic mobility of $Na^+ < Ag^+$, the conductivity slightly decreases when precipitation is complete; further addition of Na_2WO_4 results in an increase of conductivity (Fig. 1). (The ionic mobilities of Ag^+, Na^+ and NO_3^- are 63.5, 50.9 and 70.6 respectively.) In reverse titrations (Fig. 2), the conductivity rises from the beginning as the ionic mobility of $2NO_3^- > WO_4^{2-}$, and after complete precipitation it further increases due to excess of $AgNO_3$. In very dilute solutions (0.002 *M*-Na_2WO_4 and 0.01 *M*-Ag) the conductivity due to solubility of Ag_2WO_4 interferes with the results. The solubility of Ag_2WO_4 is 0.0266 g./litre and the solubility product on determination is found to be 6.12×10^{-12} at 27°.

Definite amounts of solutions of Na_2WO_4 of known strengths were brought to various p_H values by suitable additions of HNO_3 and the p_H was measured by using a glass electrode. The tungstate ion is said to exist in the different states of aggregation, depending on the p_H of the medium, according to Jander *et al.* (*Z. anorg. allgem. Chem.*, 1951, **265**, 244). When $AgNO_3$ is added to Na_2WO_4 at a p_H range from 5.5 to 6.5 and more acidic range 4 to 5, respectively and the conductance measured and plotted against the volume of the titrant, one distinct break is obtained in both cases, corresponding to the formation of $Ag_2O.2WO_3$ and $Ag_2O.4WO_3$ respectively. In each case the precipitated silver tungstate was analysed for Ag and W contents by standard methods of analysis. The compounds were found to have the same composition. No precipitation on addition of $AgNO_3$ took place below p_H 4.

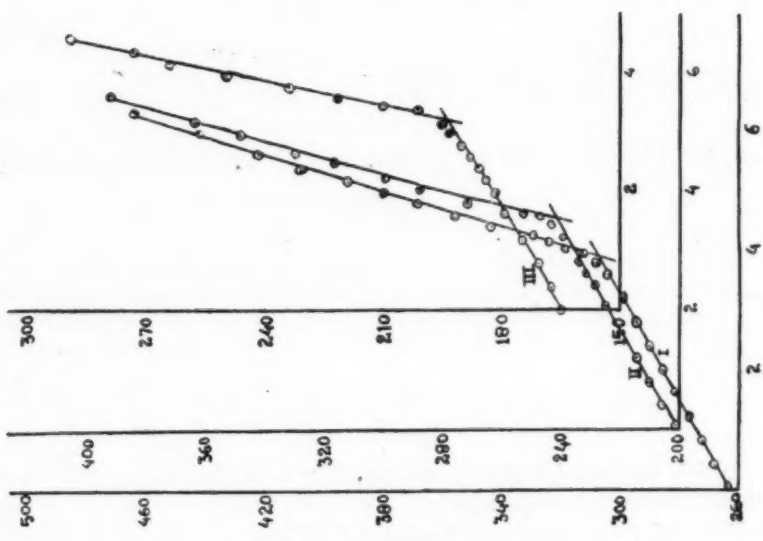


FIG. 2
Reverse conductometric titration.

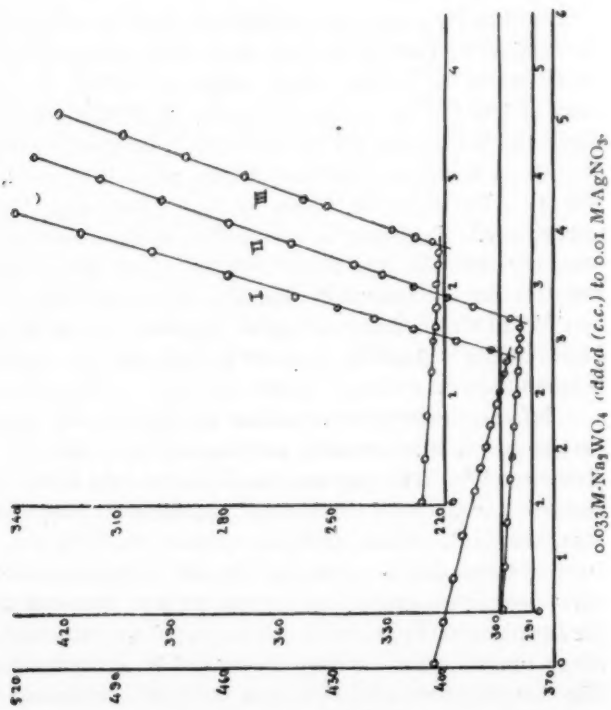
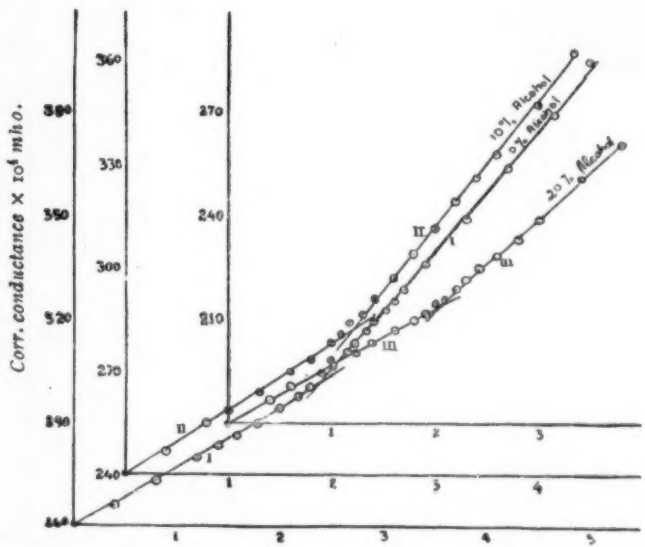


FIG. 1
Direct conductometric titration.

FIG. 3

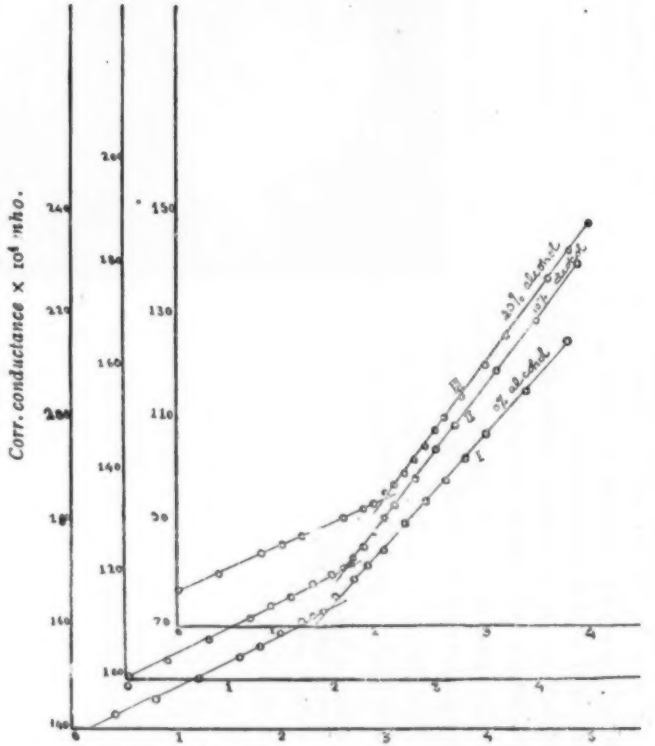
p_H = 6.0.



0.2M-$AgNO_3$ *added (c.c.) to* 20 *c.c. of* 0.025M-Na_2WO_4 *containing* 1 *mol. of acid.*

FIG. 4

p_H = 4.61.



0.2M-$AgNO_3$ *added (c.c.) to* 0.05M-Na_2WO_4 *containing* 1.5 *mol. acid.*

It may further be noted (Table 1) that the values in aqueous-alcoholic media gradually approach the theoretical values. The silver tungstate is colloidal in nature. The role of alcohol is to decrease the solubility of the precipitate and, hence, a closer approach to the theoretical values is envisaged in the experimental results, when titrations are performed in aqueous-alcoholic media.

The analytical work on the composition of various silver tungstates is under investigation and the results will be communicated later.

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CHEMICAL LABORATORIES,
GOVERNMENT COLLEGE,
KOTA (RAJASTHAN).

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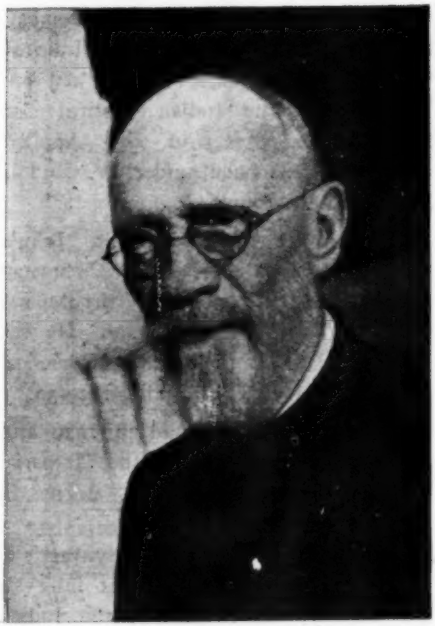
OBITUARY

Rev. Father John Van Neste, S.J.

Born: 1878 Died: Dec. 1, 1956.



Rev. Father John Van Neste, S.J., came over half-a century ago to India as a Belgian Jesuit missionary. He spent the greater part of his life at St. Xavier's College in Calcutta. For well nigh forty years Father Van Neste, as he had been generally known amongst the student community over a long period, presided over the Chemistry Department of the St. Xavier's College, watching generations of Indian graduates in science streaming out of his College in the wider horizons of life and activity.

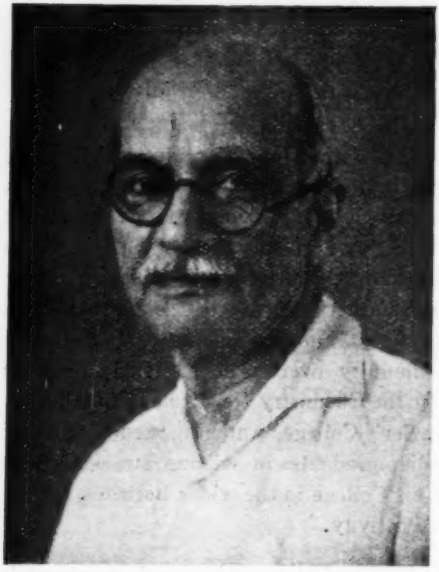
He loved his teaching work passionately and unless prevented by illness he never fought shy of his teaching task. Only when he was seventy, and his health became indifferent, he was compelled to curtail his teaching. About three years ago due to exigencies of circumstances he gladly took honours classes simultaneously for several weeks in physical, organic and inorganic chemistry, and equally efficiently.

He was a true born catholic, both by nature and tradition. In dealing with students and teachers alike, he knew no distinctions of colour, race or religion. Among the European missionary teachers in India, his popularity is no less than that enjoyed by late Rev. Father Power of the same College.

On account of his multifarious missionary duties Rev. Father Van Neste could not devote his time to researches personally, he had nevertheless a great admiration and attraction for it. As soon as the Indian Chemical Society came into existence, he became a Foundation Fellow. He served as a member of the Council for two terms. Father Van Neste was a familiar figure at most of the ordinary meetings of the Society for nearly 30 years; he took active part in their deliberations and presided over some of them.

Dr. Kantilal Chhaganlal Pandya

Born: Aug. 24, 1886. Died: Oct. 14, 1958.



Dr. K. C. Pandya was born at Nadiad in Gujarat in 1886. He had his early education at Junagadh and was graduated from Bahauddin College, Junagadh in 1907 with chemistry and physics as the main subjects. After obtaining his M.A. degree in chemistry of the Bombay University from Dr. Gajjar's Laboratory, Bombay, in 1910, he worked for two years at the Indian Institute of Science, Bangalore, in the Applied Chemistry Department under Dr. Rudolf and Dr. Sudborrough.

In 1913 he joined the St. John's College, Agra, as Professor of Chemistry and worked there as Head of the Department till his retirement in 1947. He was elected as Dean of the Faculty of Science of the Agra University during 1929-30.

He left for England in 1920 and worked for 3 years in the Imperial College of Science, London, under Prof. Thorpe and obtained Ph.D. degree in 1923 on his thesis on 'Ring chain tautomerism'.

He started his research work at the Agra College in 1934 on the synthesis of $\alpha\beta$-unsaturated acids and contributed no less than 60 papers, published at intervals mostly in the Journal of the Indian Chemical Society, Proceedings of the Indian Academy of Science and Journal of the Bombay University.

He inherited the gift of wielding a facile pen in Gujrati from his illustrious father, late Mr. Chhaganlal Pandya, whose celibrated Gujrati translation of Kadambari has become a classic of the Gujrati language. He composed in Gujrati numerous articles on scientific subjects and published them in various Gujrati periodicals. Some of those articles have been collected and published in two volumes under the title of Vigyan Mandir. He also edited a private Diary of Sri Govardhan Rave Tripathi, Gujrat's first novelist, under the caption of "Scrape Book. Vol. IV" in English.

Dr. Pandya was a Foundation Fellow of the Society and took active interest in the affairs of the Society. He was also associated with the Indian Science Congress Association, Indian Academy of Science and several other literary and scientific institutions.

He was a person of charming manners and very generous disposition. He was an ideal host and a sincere friend to his pupils.

He developed cancer in his stomach in 1951 and finally succumbed to the ravages of the disease in Oct. 1958 at his Bombay residence where he settled after retirement from St. John's College, Agra.

May his soul rest in peace!

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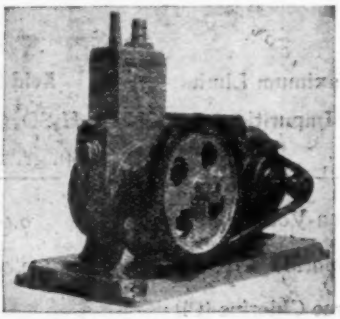

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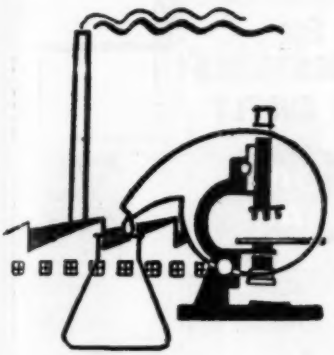

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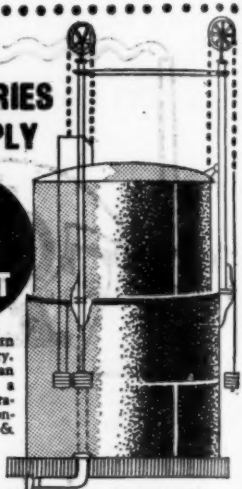

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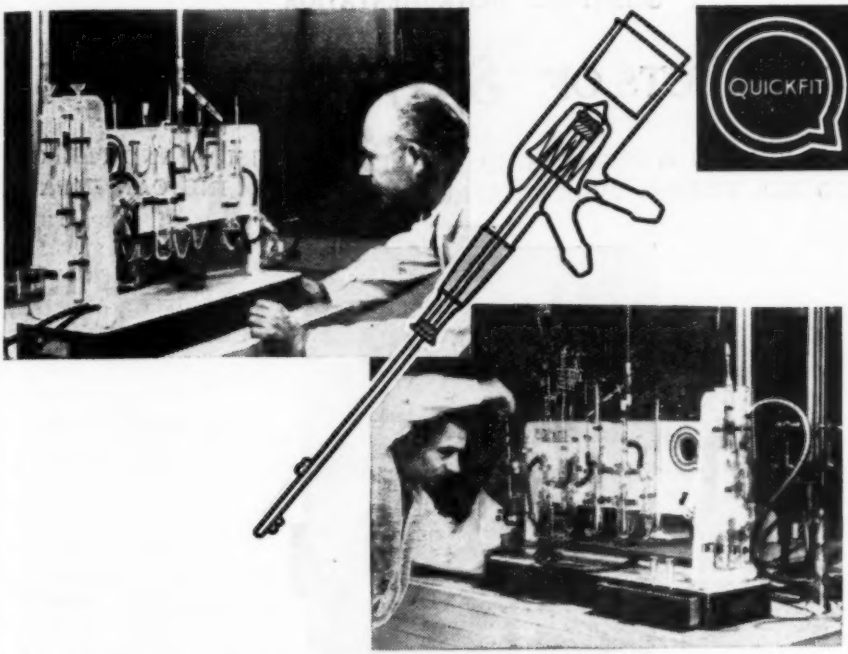

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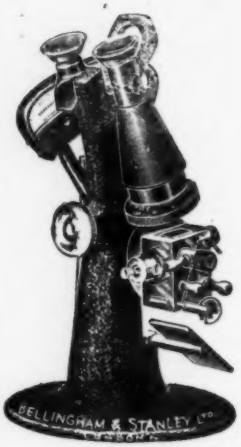

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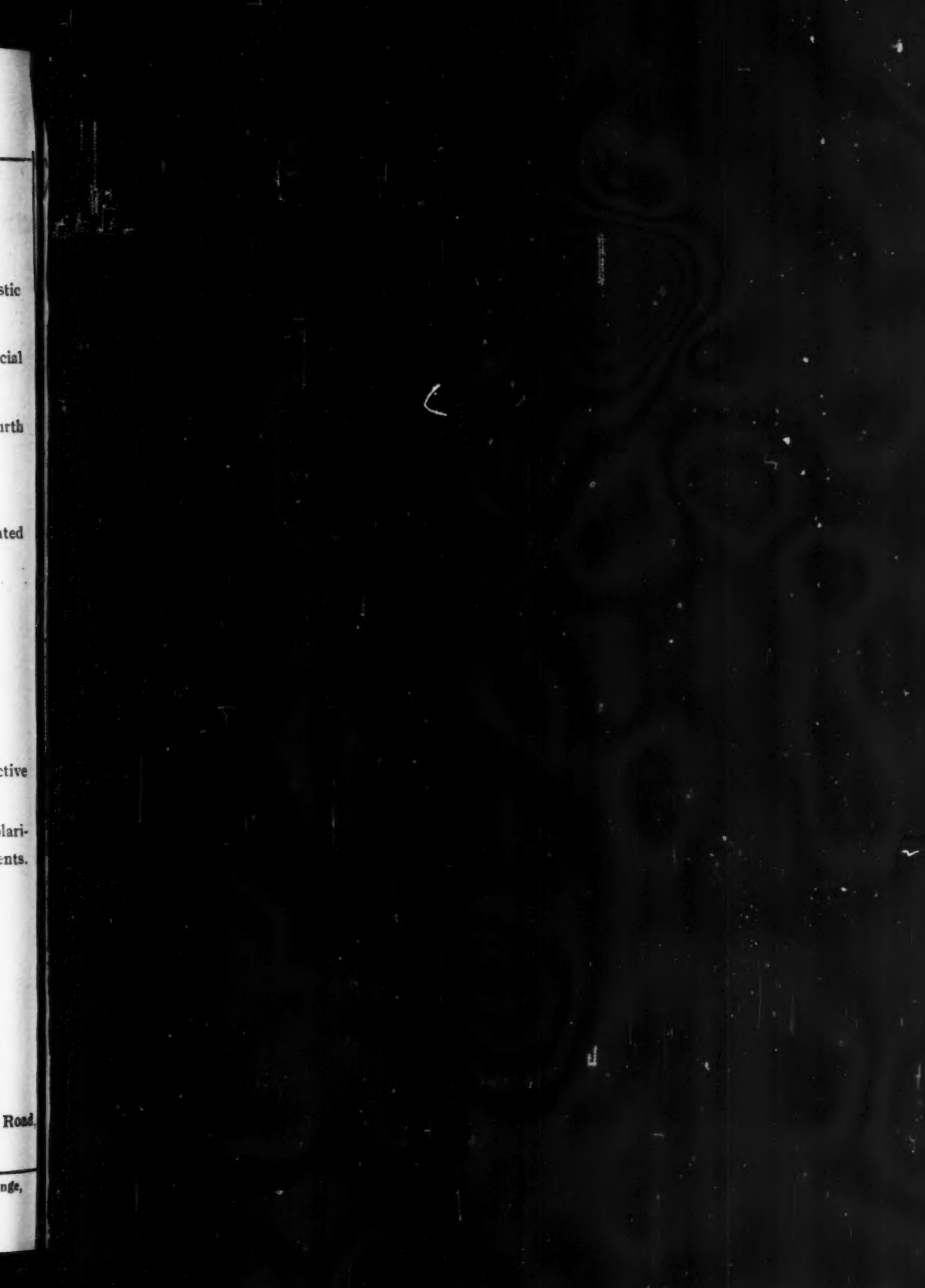
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